PHOSPHORUS CYCLING AND WATER QUALITY IN AN AGRICULTURAL WATERSHED

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ABSTRACT

Excess rural and urban nutrient inputs have led to downstream water quality degradation. Landowners in a small watershed in south central Manitoba, Canada have installed small dams as flood control mechanisms. Previous work has shown these dams and reservoirs are effective at decreasing total phosphorus (P) export, however questions of permanence, daily P fluctuation, and mechanisms influencing P retention still remain. Sediment nutrient dynamics can exert an important control on water quality on daily, monthly, and yearly timescales. To help better understand spatial and temporal patterns of P retention, P sorption assays were constructed (equilibrium P concentration or EPC_0) and compared monthly measurements of EPC_0 in small dammed reservoirs with their natural analog, stream pools. Dammed reservoirs and stream pools both showed a strong capacity to sorb P from the water column and as such, sediment processes represent a P sink across much of the catchment. *In situ* high frequency P sensors were deployed to assess short-term changes in P concentrations in four dammed reservoirs. Diel changes were only apparent later in the summer (August) but what drives these changes is unknown. Dam design to optimize nutrient retention should consider factors affecting P retention, including sediment geochemistry, but also residence time, and water chemistry as potential controls on P sorption. Diel sampling results suggest that water quality monitoring regimes that rely on singular grab samples should aim to sample in the mid-morning, especially later in the summer, so as to not over or underestimate P concentrations in water bodies.

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LIST OF ABBREVIATIONS

ANOVA	analysis of variance
A_w	artificial stream water
BMP	beneficial management practice
Ca^{2+}	calcium ions
CI	confidence interval
OMS	organic matter in sediment
CV	coefficient of variation
Cycle-P	WetLabs Cycle-PO_4 dissolved phosphate analyzer
DO	dissolved oxygen
DOC	dissolved organic carbon
EPC_0	equilibrium phosphorus concentration
EPC_{sat}	equilibrium phosphorus relative saturation
IM	initial mass isotherm
K_d	distribution coefficient
m	partition coefficient
Mg^{2+}	magnesium ions
P	phosphorus
SRP	soluble reactive phosphorus
RE	amount of phosphorus sorbed or released with respect to sediment dry weight
RM-ANOVA	repeated measured analysis of variance
RSP	reactive sediment pool
STC	South Tobacco Creek
S_w	ambient stream water
TCW	Tobacco Creek Watershed
TP	total phosphorus
X_i	amount of phosphorus sorbed or released with respect to dry weight regressed against initial phosphorus added

CHAPTER 1: GENERAL INTRODUCTION

Sustaining surface water quality is essential to decrease risks to human health and water quality degradation (Davies and Mazumder 2003). A big challenge to surface water quality is eutrophication, caused by excess nutrient inputs. These excess nutrients can cause algal blooms that can be toxic and impact fisheries, industry, tourism, and drinking water (Correll 1998). There is a need for policy and practices to help mitigate nutrient loadings into areas sensitive to eutrophication.

On the agriculturally driven Canadian prairies, Lake Winnipeg, located in Manitoba, Canada faces continued increases in nutrients. Phosphorus (P) export to the lake has doubled in the ten year span from 1990-2000 (McCullough et al. 2012) and cyanobacteria blooms have doubled in size since the mid-1990s (Kling et al. 2011, Scott et al. 2011). Many factors attribute to increased P export to Lake Winnipeg, however much of the focus has turned to decreasing agricultural outputs in the Red River Watershed (Glozier et al. 2006, Schindler et al. 2012).

Attempts to decrease the amount of P exported from the Red River watershed have started in the smaller headwater tributaries where beneficial management practices (BMPs) have been put into place in an attempt to regulate nutrient outputs and flooding (Tiessen et al. 2011). However, in snowmelt dominated regions, such as the Canadian prairies, BMPs must be able to cope with the large pulse of water that occurs during the spring melt (Li et al. 2011).

In a small portion of the Red River Watershed, the Tobacco Creek watershed, located ~150 km southwest of Winnipeg, a local landowner group has installed small dams in an attempt to both decrease downstream flooding events, through temporary water storage, and decrease nutrient flow downstream through nutrient retention (Tiessen et al. 2011). The head water dams at Tobacco Creek decrease annual total phosphorus (TP) exports downstream (Tiessen et al. 2011). This potential for small dams to decrease annual TP loads has led to questions surrounding the fate, permanence, and mechanisms of P retention in the reservoirs.

Numerous mechanisms inside and outside of small dams and resulting reservoirs contribute to P retention and release in aquatic systems on yearly, monthly, and daily time scales. Autotrophic uptake and assimilation, sediment uptake and release, and sedimentation have all been shown to affect P concentrations in the water column (Reddy et al. 1999). In particular many studies have focused on buffering of P concentration from the water column by sediments (Froelich 1988, Grobbelaar and House 1995, Jarvie et al. 2005, Lottig and Stanley 2007, Lai and

Lam 2009, McDaniel et al. 2009). Sediments act as either a sink of P or source of P to the water column depending on the P equilibrium dynamics within the sediments and the overlying P concentration in the water. Characterizing P sediment interactions can be a valuable tool when evaluating P retention mechanisms and the permanence of P retention within watersheds.

Daily fluctuations in P, if present, are thought to be related to biological activity. These changes may also suggest important short-term controls on P retention are at play. Daily changes in P are rarely studied (Nimick et al. 2011) and past work has been limited to large river systems (Scholefield et al. 2005, Sherson et al. 2012, Cohen et al. 2013). Recent advances in *in situ* water quality monitoring have made determining daily changes a more manageable task. However, there is disagreement within the literature as to the factors influencing daily P fluctuations (Volkmar et al. 2011, Sherson 2012, Cohen et al. 2013) which have led to more question surrounding drivers of daily changes in P, and the potential importance of daily changes in understanding watershed export.

This thesis looks to identify controls on phosphorus retention in constructed headwater dams. These dams are contrasted with seven stream pool sites further downstream to determine if reservoirs differed in P dynamics from depositional stream pools (their natural analog) to help further understand controls on P dynamics between reservoirs and stream pools, and vulnerability to changing environmental conditions. This work is extended to include a methods validation for assessing P sorption dynamics. The second part of the thesis focuses on the intensive study of four reservoirs in which high frequency phosphorus sensors were deployed. The phosphorus sensors were used determine whether 24-hour changes in phosphorus dynamics were occurring and to further understand P dynamics and cycling on short time scales. Understanding both long and short-term P dynamics and export in small watersheds is important for developing a better understanding the effectiveness of BMPs in controlling downstream nutrient transport.

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CHAPTER 2: EFFECTS OF SEDIMENT AND WATER QUALITY PARAMETERS ON PHOSPHORUS CHEMISTRY

Sediment-nutrient dynamics can exhibit an important control on water quality. In the Tobacco Creek Watershed (TCW), Manitoba, Canada, questions have arisen regarding how phosphorus is cycled in small reservoirs built for flood control and nutrient retention. To determine the role of sediments in mediating water chemistry, we obtained water and sediment samples from eight reservoirs and seven downstream stream pools. Equilibrium phosphorus concentration (EPC_0) was measured through adsorption/desorption batch equilibrium methods. The goals of this work were to assess sediments role in buffering phosphorus, and to determine if small constructed reservoirs differ from their natural analog of stream pools in their sediment phosphorus dynamics. We characterized key predictors of equilibrium phosphorus concentrations while examining factors affecting the stability of P retaining compounds and assessed the suitability of artificial water mixes in predicting ecologically relevant equilibrium phosphorus concentrations. Sorption characteristics between reservoirs and stream pools were not significantly different and a large degree of spatial and temporal variability was observed across the watershed; however sorption characteristics significantly differed when divided geographically, on and off the escarpment. Dissolved organic carbon, calcium ions, alkalinity and organic matter in sediment were all important predictors of P sorption. Site specific artificial water, with calcium and magnesium concentrations reflective of *in situ* conditions, was determined to be a suitable alternative to natural stream water when predicting EPC_0 values in this study. Future small dam beneficial management practices should aim to maximize water sediment interactions to encourage P sorption from the water to sediments.

2.1 Introduction

Water quality deterioration due to increased nutrient loading is a global problem and the Canadian prairies are no exception. The 10th largest freshwater lake in the world, Lake Winnipeg in the province of Manitoba, is of particular interest. The aquatic health of Lake Winnipeg has decreased over the past 30 years (Lake Winnipeg Stewardship Board 2006) with concern focused on elevated nitrogen and phosphorus (P) loading from urban and agricultural sources (Glozier et al. 2006, Lake Winnipeg Stewardship Board 2006). It has been estimated that as much as 15% of the P loadings to Lake Winnipeg come from agricultural practices within Manitoba (Lake Winnipeg Stewardship Board 2006).

In catchments of the Canadian prairies, meeting water quality targets will require altered management to control agricultural nutrients. In order to mitigate P loadings, many farmers have introduced beneficial management practices (BMPs), practices that not only benefit the environment but are also practical and benefit those implementing them, such as small dams and resulting reservoirs, riparian buffer strips, or changes in tillage practices. One management option of considerable interest is the use of small, constructed reservoirs (Tiessen et al. 2010, Li et al. 2011, Tiessen et al. 2011). These reservoirs can help mitigate flooding, and can be effective nutrient sinks in snowmelt-dominated landscapes where many other beneficial management practices (e.g. riparian buffer strips), are thought to be ineffective due to the timing of nutrient transport (Nigel et al. 2014). In the Tobacco Creek Watershed, an agricultural area in south-central Manitoba, a local landowner group has installed 50 small headwater dams (average depth 1.8 m; average storage 19,000 m^3), with construction beginning in 1985 (Yarotski 1996). Previous work on these dams has shown that not only do they decrease peak flows during snowmelt and rain events, but they also increase nutrient retention (Tiessen et al. 2011).

Phosphorus is the primary limiting nutrient in freshwater systems (Schindler et al. 1977) and as such, there is significant interest in understanding phosphorus transport and retention within catchments. Evidence from urban-influenced systems suggests that in-stream processes may have a critical control on rates of P export (Jarvie et al. 2005; Jarvie et al. 2008; Palmer-Felgate et al. 2009). There are numerous mechanisms that can lead to P retention, or release in aquatic ecosystems, including autotrophic uptake and assimilation, sediment uptake/release, and sedimentation in depositional areas, such as stream pools (Reddy et al. 1999). Both dissolved organic and inorganic P interact strongly with sediment (Grobbelaar and House 1995), and

sediment dynamics can have a large impact on P dynamics. In streams and ponds, ecological metabolism, influencing pH and dissolved oxygen (DO), and ionic strength affect the chemical composition of P complexes and consequently affect the sorption and desorption of P by sediments (Fytianos and Kotzakioti 2005). Generally, during sediment buffering, P is absorbed when the concentration in the water column is higher than the P concentration in the sediment pore water (Lai and Lam 2009). Importantly, this means that nutrient mitigation efforts can induce desorption of sediment P pools, slowing recovery from eutrophication as sediments and water reach a new equilibrium (Jarvie et al. 2005).

The vulnerability of sediment phosphorus to release is dependent upon compounds in which P is stored. The most common inorganic P forms are in combination with iron, manganese, calcium, magnesium, and aluminum (iron oxyhydroxides, manganese oxyhydroxides, apatites, magnesium struvites, and aluminum variscites respectively) (Golterman 2004). Iron hydroxides and oxyhydroxides are sensitive to changes in DO (Shenker et al 2004, Hupfer and Lewandowski 2008). If exposed to suboxic (< 1.0 mg O_2 L^{-1}) and anoxic (<0.3 mg O_2 L^{-1}) conditions, the normally strong binding of oxyhydroxides weakens, and the phosphate will diffuse back to the system (Grobbelaar and House 1995, Correll 1998, Erickson et al. 2012). At high pH (>7.5), calcium and magnesium phosphate compounds can precipitate from the water column, decreasing P availability for biologic uptake, however low pH (<6.5) conditions facilitate release of P from calcium and magnesium phosphates (Burns et al. 2001, Lukkari et al. 2007). Conversely, aluminum phosphate compounds precipitate at low pH (<6.5) and form extremely strong bonds (Reddy and DeLaune 2008). Changes in pH and DO that are naturally induced by photosynthetic processes may have a large impact on how much P is available for uptake, and on which species of P are sequestered in compounds that precipitate out of the water column.

Many farmers in the Tobacco Creek Watershed have introduced small dams as beneficial management practices (BMPs). These small reservoirs share many physical properties in common with ponds, due to the fact that during most of the summer water does not flow out through the drop inlets. Phosphorus can be retained in ponds and small wetlands in numerous ways, including in vegetation and microorganisms, via sorption with sediments, chemical precipitation, and via sedimentation (Reddy et al. 1999, Burford et al. 2011). The construction of dams creates areas of water with long residence time, and slow flow of water, enhancing

sedimentation rates, and allowing time for increased interaction between sediment and P compounds in the water (Burford et al. 2011). Phosphorus retention within headwater dams helps to decrease downstream loading; however, the chemical speciation of P, and its long-term fate in agricultural reservoirs, is not well characterized. Sediment P pools can be remobilized with changing environmental conditions, including changing pH or DO in overlying water concentrations. Further understanding of how sediments may mediate the source/sink dynamics of stream pools and reservoirs will aid our understanding of catchment scale nutrient dynamics and the permanence of P retention in BMPs.

In this study, we investigated the P dynamics of 8 reservoirs, and 7 natural stream pools to determine whether sediments were acting as a net source or sink of phosphorus, assess whether constructed reservoirs differed in their P dynamics from their natural analog (depositional pools), identify the major species of sediment P to help understand their vulnerability to changing environmental conditions (pH, O_2), and identify differences between these two site types that may affect nutrient dynamics. We assess source-sink dynamics using equilibrium phosphorus concentration (EPC_0) assays. In this method, sediments are incubated in contact with artificial water made to mimic stream water (Nair et al. 1984, Froelich 1988, Lottig and Stanley 2007, McDaniel et al 2009). Methods in the literature vary in terms of ways to simulate natural stream water, so to help assess the validity of the approach, we test the suitability of artificial water-based approaches, and discuss the use of both artificial water and ambient stream water in methods to evaluate EPC_0.

2.2 Materials and Methods:

2.2.1 Study Area

The Tobacco Creek Watershed is situated ~150 km southwest of Winnipeg and drains ~1000 km^2 of agricultural land. This watershed covers parts of Lorne, Thompson, and Roland Rural Municipalities of Manitoba. Tobacco Creek, an ephemeral creek, is unique in the fact that the creek begins west of the Manitoba Escarpment at an elevation of 320 m and flows eastward down the escarpment, losing an elevation of around 60 m in less than 3 km. The area spans the transition zone from the higher elevation Saskatchewan Plain to the lower Manitoba Plain (Tiessen et al. 2011). The climate in this region is characterized by short summers and long cold winters, with an annual mean temperature of ~3º C (Environment Canada 2009). In 2013 peak snowmelt occurred in late April.

Three types of dams have been installed in the Tobacco Creek watershed between 1985-1996. The first are dry dam and flood control dams (Yarotski 1996). These dams fill with water and then drain continuously through a drop inlet drain. The second are back-flood dams which retain a shallow amount of water over a large field until the water is released and drains completely (Yarotski 1996). The third type are multipurpose dams which fill and drain similarly to the dry dams, however a base level of 20% of the full storage capacity is retained for water use throughout the summer (Tiessen et al. 2011). All of the dams in the present study were either dry dams or multipurpose dams.

Water and sediment samples were taken from 15 sites throughout the watershed (Table 2.1; Figure 2.1; Figure A.4). Eight sites were small reservoirs and seven sites consisted of downstream depositional areas (stream pools) of the stream that are characterized by low flow through most of year with flow typically stopping in late summer (Buttle et al. 2012). Due to the large amount of rain throughout the summer of 2013 (average ~440 mm, farmer network monitoring data, Don Cruikshank, personal communication, 24 September, 2014), five stream pool sites continued to show some flow through summer.

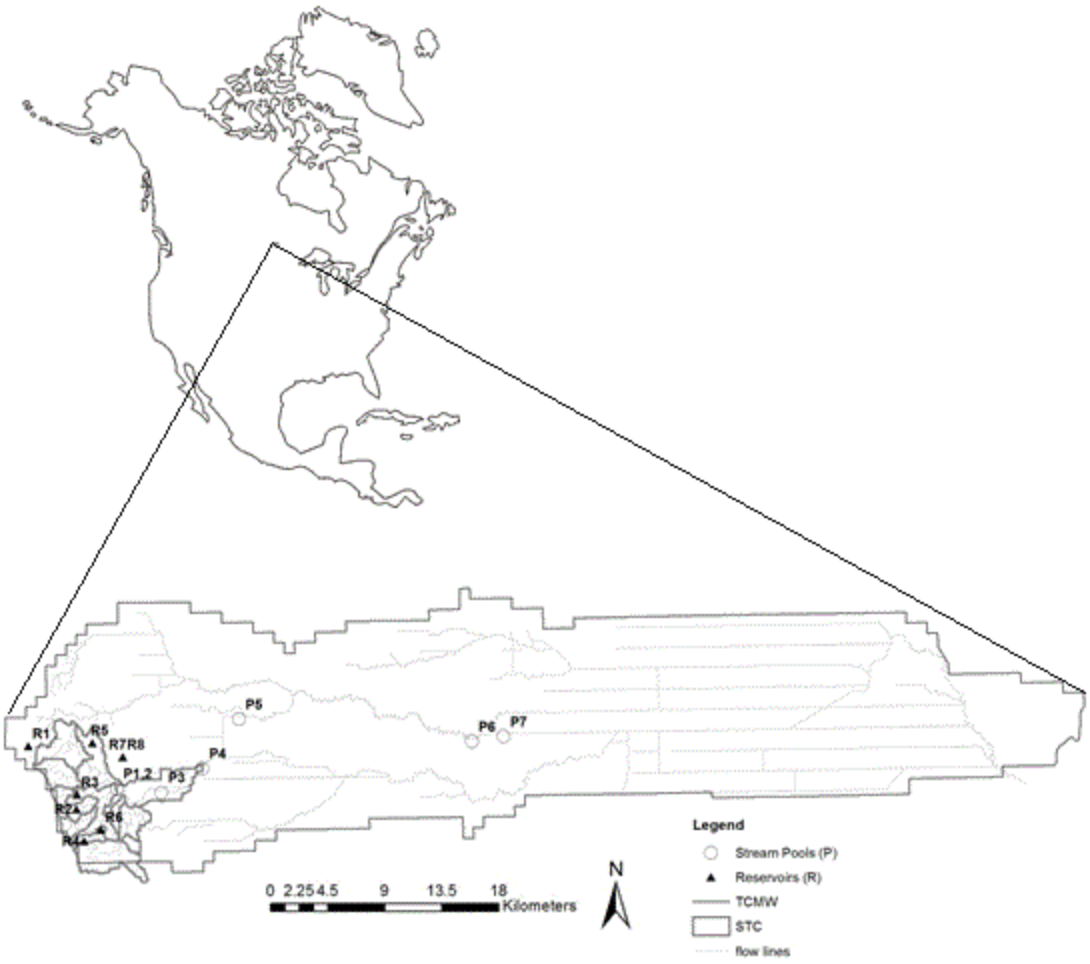

Figure 2.1. Tobacco Creek Watershed (TCW). The dark gray outline within the TCW is the South Tobacco Creek watershed (STC). The location within North America is also shown.

Table 2.1. Summary of sample sites.

Code	Coordinates	Reservoir Type	Reservoir Area (km^2)	Reservoir depth (cm)
R1	49º 23’ 45” N 98º 26’ 21.7”W	Multi-purpose	No information	120
R2	49º 21’ 2” N 98º 23’ 15” W	Multi-purpose	0.008	97
R3	49º 21’ 47” N 98º 23’ 12” W †	Dry	0.03	210
R4	49º 19’ 40” N 98º 22’ 45” W	N/A	0.004	11
R5	49º 23’ 52” N 98º 22’ 11” W	Multi-purpose	0.013	91
R6	49º 20’ 10” N 98º 21’ 38” W †	Multi-purpose	0.023	1.95
R7	49º 23’ 25” N 98º 20’ 11” W	Dry	No information	217
R8	49º 23’ 4” N 98º 19’ 53” W	Dry	No information	192
P1	49º 21’ 55” N 98º 20’ 37” W	N/A*	N/A	N/A
P2	49º 21’ 55” N 98º 20’ 37” W ‡	N/A*	N/A	N/A
P3	49º 21’ 44” N 98º 17’ 42” W	N/A*	N/A	N/A
P4	49º 22’ 44” N 98º 15’ 0” W ‡‡	N/A	N/A	N/A
P5	49º 24’ 50” N 98º 12’ 35” W	N/A*	N/A	N/A
P6	49º 23’ 45” N 97º 57’ 23” W	N/A	N/A	N/A
P7	49º 23’ 57” N 97º 55’ 20” W	N/A*	N/A	N/A

* Denotes stream pools that continued to flow throughout the field season.
† Denotes sites studied in Tiessen et al. 2011.
‡ Denotes previous Environment Canada water monitoring site
‡‡ Denotes current Environment Canada water monitoring site

2.2.2 Sample collection and *in situ* measurements

Water and sediment samples were collected during May, June, July, and August 2013 in head water dams and stream pools, in the Tobacco Creek watershed. Temperature, dissolved oxygen (DO), pH, and conductivity were recorded at each site using a Thermo Scientific Orion, Orion 8107 UWMMD Ross Ultra pH/ATC Triode (Thermo Scientific). Unfiltered water samples (1 L) were collected via dip sampling and frozen for future analysis. In addition, 50 mL and 35 mL unfiltered water samples were collected for alkalinity and total phosphorus analysis, respectively. All sediments were collected in the same identified area of each site (marked by GPS point) throughout the field season by hand coring (5 cm diameter core, 0-5 cm depth into the sediment) at a water depth of ~45 cm ±10 cm. In the headwater dams, sediments were collected in transects parallel to the shoreline with additional transects following a perpendicular path towards the middle of the reservoir. Transects were followed across the stream pools. If it was not possible to make an entire transect across the stream pool, the transect pattern used for reservoirs was applied (Appendix A, Figure A.3). Sediment samples were pooled together for a representative sample. Where possible, sediment samples were analyzed immediately; however

subsets of samples were frozen until analysis. Freezing tests indicated no significant impact on results (Appendix A, Figure A.1, two sample t-test, p=0.32).

2.2.3 Water Chemistry Parameters

2.2.3.1 Soluble Reactive Phosphorus (SRP) and Total Phosphorus (TP)

Thirty-five mL water samples were syringe filtered with 25 mm minisart-plus non-sterile 0.45 µm (cellulose acetate) +GF prefilter (Fisher Scientific, Ottawa Ontario) into 50 mL glass vials for soluble reactive phosphorus analysis (SRP). An additional 35 mL unfiltered sample was collected for Total Phosphorus (TP) analysis. Soluble reactive phosphorus and TP were kept on ice and analyzed via the molybdate blue method ascorbic acid technique, EPA method 365.1 (Murphy and Riley 1962, O'Dell 1993) using a UV-1601PC UV-Visible spectrophotometer (Shimadzu, Laval, QC). SRP and TP analyses were completed within 36-48 hours and 30 days, respectively. Total phosphorus samples were digested with a 3% potassium persulfate solution in an autoclave for 45 minutes at 121 °C before analysis (Manzel and Corwin 1965, Wetzel and Likens 1991).

2.2.3.2 Equilibrium Phosphorus Concentration (EPC_0)

A common means of assessing source/sink dynamics of sediments is the use of equilibrium phosphorus concentration (EPC_0) batch sorption equilibrium experiments. These *ex situ* experiments involve equilibration of sediment with modified standard artificial water to determine the point (EPC_0) where there is no net release or adsorption of P from overlying water (Nair et al. 1984, Froelich 1988, Lottig and Stanley 2007, McDaniel et al 2009).

P release and adsorption occurs in two phases, a rapid surface adsorption (desorption) stage that can occur between minutes and hours, the sorption observed in EPC_0 experiments, and a separate longer permeating (release) phase that can last from days to years (Barrow 1983). Most researchers ignore the second longer step and measure P sorption after a known amount of time, approximately 24 hours, because the sorption process can be considered near complete at this time (House et al. 1995). This measure is assumed to be close to equilibrium and therefore a viable measurement for estimating P sorption (House and Denison 2000, Jarvie et al 2005, Lottig and Stanley 2007, Belmont et al. 2009, Bhadha et al. 2012).

Artificial stream water (A_w) is made to mimic the general pore water ionic strength of the sample study area. Common additives for artificial stream water include KCl (Bhadha et al. 2010), $CaCl_2$ (Nair et al. 1984, Lottig and Stanley 2007, Bhadha et al. 2012), and $MgCl_2$ (Lottig

and Stanley 2007). In general, as ionic strength of the water increases due to additions of K^+, Ca^{2+}, and Mg^{2+}, so does P sorption, due to additional binding sites for the negatively charged phosphate ion (Nair et al. 1984). As important as ionic strength is for estimating EPC_0 values it is important to remember that negatively charged organic ions such as hydroxyl ions, found in natural stream water, can compete for binding sites with P (Lijklema 1980, Reddy and Delaune 2008).

Since many of these competitors cannot be controlled, or may not be present in laboratory experiments, care should be taken not to overestimate pore water ionic strength in study sites, typically the sole external factor controlled for. In previous studies (Jarvie et al. 2005, Palmer-Felgate et al. 2009, Bhadha et al. 2010, Bhadha et al. 2012), standard amounts of buffering ions have been added to make artificial water that mimics general study area pore water ionic strength; however, spatial differences that may occur are often ignored. Some researchers have used natural stream water to help avoid the issue of ionic strength as well as other water quality parameters that may influence EPC_0 (Dunne et al. 2006, McDaniel et al. 2009, Machesky et al 2010), but this approach is typically limited to systems where SRP concentrations are less than EPC_0.

As to not over or under estimate EPC_0 sorption capacity of the sediments of Tobacco Creek, EPC_0 experiments were performed using an artificial water (A_w) solution with individual site specific Ca^{2+} and Mg^{2+} concentrations, an expansion of the approach followed by Lottig and Stanley (2007) who used specific concentrations to mimic the whole study area. Concentration of Ca^{2+} and Mg^{2+} were measured by Flame Atomic Absorption Spectroscopy at Trent University and the University of Saskatchewan (Analytical methods for atomic absorption spectroscopy instruments 1996) on collected water from each individual study site throughout the field season (see Appendix A; Table A.1 for data).

Site specific artificial water (A_w) mixes were then spiked with a 100 mg L^{-1} phosphorus stock solution made from dibasic potassium phosphate, (K_2HPO_4 (Fisher Scientific, Ottawa Ontario)) to make 6 phosphorus concentrations 0, 0.05, 0.1, 0.5, 1 and 2 mg L^{-1}. Each water mix (15 mL) was added to 2-4 g of wet sediment (dry weight equal to 1.5 g) to create a slurry in pre-weighed 0.05 L falcon tubes (Fisher Scientific, Ottawa, Ontario). Chloroform was added to inhibit microbial activity (75% Ethanol (Fisher Scientific, Ottawa, Ontario), Lottig and Stanley 2007). The tubes were placed horizontally on an orbital shaker table at 190 rpm for 24 hours at a

temperature of 15 °C. Following the experiment, samples were centrifuged for 15 minutes at 3500 rpm, the supernatant was filtered (0.45 μm MCE syringe filter (Fisher Scientific, Ottawa Ontario)), and analyzed by the molybdate blue ascorbic acid technique, EPA method 365.1, on the SmartChem 170 discrete chemistry analyzer (Unity Scientific, Brookfield, CT; Murphy and Riley 1962, O'Dell 1993). Phosphorus that was not recovered in the analyzed filtrate was assumed to be retained by the sediment. These data can then be used to identify times, or locations of net sediment P release (EPC_0 > SRP) or uptake (EPC_0 < SRP). Single experiments were run for most occasions, with a single site (eg. P1, August 2013) analyzed in triplicate to assess experimental error. The coefficient of variation (CV) for the replicates was 7.4% (Appendix A, Figure A.2). Sorption, normalized to sample dry weight, was regressed against the initial concentration of phosphorus. EPC_0 values, corresponding to net sorption/desorption equal to zero, were calculated as the x-intercept of the regression line.

To determine sediment affinity for P sorption and assess the amount of native phosphorus sorbed, the linear initial mass isotherm (Nodvin et al 1986) was applied. The initial mass (IM) isotherm is well suited for natural systems where the sorbate in question is already present (Nodvin et al 1986, Vance and David 1992, McDaniel et al. 2009). The IM is calculated by regressing the amount phosphorus sorbed or released (mg) with respect to dry weight (RE) against the initial phosphorus added (mg) with respect to dry weight (X_i). The resulting equation is as follows (all units in mg P kg^{-1}):

$$RE = m \times X_i - b \tag{2.1}$$

The slope (m) is a unitless measure representing the partition coefficient; a fraction of the total reactive substance in a sediment/water system that is retained by the sediment. The y intercept (–b) corresponds to the value of the amount desorbed when $X_i = 0$, the point of 0 mg L^{-1} initial phosphorus with respect to dry weight.

Two other coefficients describing sorption affinity can be calculated from IM. The first, the reactive sediment pool (RSP), is the calculated value of the reactive substance present in the sediment with respect to weight. RSP (mg P kg^{-1}) is calculated as follows:

$$RSP = \frac{b}{(1-m)} \tag{2.2}$$

The second coefficient is the distribution coefficient (L kg^{-1}); commonly referred to as K_d. K_d measures the affinity of P for the sediments with respect to the solution volume and sediment dry weight. K_d (L kg^{-1}) is calculated as follows:

$$K_d = \frac{m}{(1-m)} \times \frac{solution\ volume}{sediment\ mass} \quad (2.3)$$

2.2.3.3 EPC_0 Relative Saturation

EPC_0 and SRP values were used to determine an EPC_0 Relative Saturation (EPC_{sat}), which is defined as:

$$EPC_{sat} = 100 \times \frac{(EPC_0 - SRP)}{EPC_0}$$ (Jarvie et al 2005). (2.4)

Negative values of EPC_{sat} correspond to the sites' potential for phosphorus (SRP) uptake whereas positive values correspond to the sites' potential for phosphorus (SRP) release. Saturation values were non-normal, therefore to determine differences between months, a non-parametric Kruskal-Wallis test was used.

2.2.3.4 Alkalinity

Unfiltered water samples were collected in 0.05 L falcon tubes (Fisher Scientific, Ottawa, Ontario) and preserved on ice. Samples were filtered in lab by vacuum filtration with 0.7 μm glass fiber filter (Fisher Scientific, Ottawa, Ontario) and analyzed within 30 days on the TitraMaster 85 (Hach, Loveland, Colorado).

2.2.3.5 Dissolved Organic Carbon (DOC)

Water samples for DOC analyses were filtered with a Geotech peristaltic pump through ashed 0.7 μm glass fiber filters (Fisher Scientific, Ottawa, Ontario). Water was stored at 4° C until analysis. Samples were analyzed on the Total Organic Carbon Analyzer (TOC-V_{CPN} (Shimadzu, Laval, QC)) at the University of Saskatchewan Soil Science Laboratory.

2.2.3.6 Organic Matter Content in Sediment (OMS)

Organic matter content was quantified by the loss on ignition technique (Schumacher 2002). Extra sediment that was collected for EPC_0 analysis was subsampled and stored at 4° C until analysis. Sediment samples were dried in a desiccator to a constant weight. Ten grams of dried sediment was placed in a ceramic crucible and combusted at 400° C for 12 hours. Once complete, samples were placed back in the desiccator to cool and were weighted again. The equation to determine percentage of carbon content is:

$$\%\ organic\ matter\ content = \frac{(mass_{initial} - mass_{final})}{mass_{initial}} \times 100 \quad (2.5)$$

2.2.3.7 EPC_0: Ambient stream water

Ambient stream water (S_w) was used to determine if different water chemistry parameters other than Ca^{2+} and Mg^{2+} concentrations were important in determining an EPC_0 (Meyer 1979).

In sites where the EPC_0 value was greater than the SRP value, EPC_0 could also be run with ambient S_w. Water was thawed overnight and measured for SRP via SmartChem 170 (Unity Scientific, Brookfield, CT) using EPA method 365.1 (ascorbic acid technique based on Murphy and Riley 1962; O'Dell 1993). A stock solution (100 mg L^{-1} P, K_2HPO_4 (Fisher Scientific, Ottawa Ontario)) was used to increase site specific SRP values to match concentrations used in the A_w incubations. Analyses were continued as described for EPC_0 with A_w.

EPC_0 using ambient S_w and the corresponding EPC_0 values using A_w were log_{10} transformed to normality and compared using a paired t-test. Initial isotherm metrics, K_d, RSP, and partition coefficients, were log_{10} transformed, square root transformed, and brought to the 20^{th} power, respectively and compared using a paired t-test. In a study by McDaniel et al. (2009), EPC_0 was determined with both artificial water and ambient stream water for a subset of samples. The EPC_0 values were regressed together to generate an equation to mathematically calculate the missing samples (Warton et al. 2012; R Project, R Core Team 2013). The same approach was taken in this study to estimate EPC_0 values that could not be determined experimentally due to SRP>EPC_0. Calculated data for samples that could not be run with ambient stream water can be found in Appendix A Table A.3.

2.2.3.8 Percent variation equation

Percent variation was used to determine the variation between artificial water EPC_0 and ambient stream water EPC_0.

Percent variation between artificial water and ambient stream water was calculated as follows:

$$\%\ variation = \frac{(Artificial\ water\ EPC_0 - Ambient\ stream\ water\ EPC_0)}{Overall\ average\ SRP} \times 100 \qquad (2.6)$$

2.2.3.9 Data Analysis

A one-way RM-ANOVA was used to assess temporal differences, and habitat differences (reservoir or stream pool) in EPC_0. EPC_0 values were log_{10} transformed to normality prior to RM-ANOVA. Pearson's product moment correlations were run between EPC_0 and initial mass isotherm sorption metrics (K_d, RSP, and partition coefficient) and EPC_0 and all water quality parameters (R Project, R Core Team 2013).

Due to small sample size (reservoirs n=8; stream pool n=7) the asymptotic Wilcoxon Mann-Whitney Rank Sum permutation test was used to compare annual median values of all

water quality parameters and initial mass isotherm sorption metrics between site types (Hothorn et al. 2008; R Project, R Core Team 2013).

All water quality parameters and physical parameters were used in a best subset regression model with EPC_0 as the dependent variable, with and without SRP as a predictor variable to determine if SRP was influencing the outcome of the regression. All best subsets were analyzed using Minitab 17 Statistical Software (2010). Models were evaluated through best subset criterion and between groups ANOVAs. The three best fits for each site type were determined by the largest adjusted r^2, smallest square root of mean standard error (S), and best fit of Mallows C_P (number of parameters plus one). To identify the best model out of the possible three, an ANOVA was run. In the event of a tie, the simplest model with maximized Mallows Cp was chosen, to avoid over-parameterization.

2.2.4 Sediment physical parameters and chemistry

2.2.4.1 Particle size analysis.

Sediments were analyzed for average particle size via Laser Diffraction Technique (LA-950, University of Regina; Horiba Scientific, Burlington, ON). A 10 g subsample of sediment was air dried and sieved to 2 mm. Samples were sonicated for 90 seconds and run in triplicate. Clay and silt particles made up approximately two thirds of the sediment for each site and represents the portion most likely to interact with P (Lake and Morrison 1977); therefore, the % clay fraction and % silts were combined to obtain % fines (<0.05 mm) portion (Soil Survey Staff 1999).

2.2.4.2 Sediment Fractionation

Sediment fractionation techniques are used for the determination of P binding forms in aquatic sediments. The modified Williams (1971) method as put forth in Ruban et al. (1999), and later modified in Ruban et al. (2001) as a European Programme, Standards, Measurements and Testing protocol, was used to determine the HCl-extractable phosphorus (phosphorus bound to calcium), NaOH- extractable phosphorus (phosphorus bound to metal oxides), and total phosphorus fractions found in the sediment during the last sampling of the field season (August 2013). Interpreting extraction values was done with caution as no extraction method is exact. De Groot and Golterman (1990) showed that P initially associated with Al and Fe compounds has the potential to be sorbed by or precipitate out with Ca^{2+} minerals during the NaOH extraction. This finding was further corroborated in later studies, using similar acid/base extractions,

observing an overestimation of Calcium-P and an underestimation of metal oxide-P (Benzing and Richardson 2005, Hupfer et al. 2009) where approximately 33% of metal oxide bound P was recovered from sediments spiked with a known amount metal oxide bound P.

Quadruplicate samples were run for fractionation at three of the sites to determine precision of the method (Table A.5), while duplicate samples were run at the remaining 12 sites. All samples were acidic and were neutralized using 1 N NaOH and phenolphthalein indicator, pH paper (range 3-5.5, Fisher Scientific, Ottawa, Ontario) or pH probe (Thermo Scientific Orion, Orion 8107 UWMMD Ross Ultra pH/ATC Triode (Thermo Scientific)) to bring samples to a pH of 5. Samples were then analyzed by the molybdate blue method on the SmartChem 170 discrete chemistry analyzer (Unity Scientific, Brookfield, CT). Coefficients of variation for replicates were acceptable below 10%.

2.2.4.3 Sediment Metals

Sediments from August 2013 were analyzed for Fe, Mg, and Mn. These metals in sediment were determined through conventional hotplate aqua regia acid (HCl, HNO_3) digestion method as put forth in Chen and Ma (2001). A dried homogenized sample of 0.1000 g was weighted into 20 mL Teflon digestion vial and combined with 0.2 mL of ultra-pure water to create a slurry. 0.6 mL of HNO_3 (ACS-Pur, Fisher Scientific, Ottawa, ON) was added to the samples and after 15 minutes, 1.8 mL of HCl (ACS-Pur, Fisher Scientific, Ottawa ON) was added. Samples were slowly brought up to 85 °C on a hot plate until near dryness, or approximately three hours. Dry samples were removed from hot plate and let cool for five minutes. Once cool 4 mL of 2% HNO_3 (v/v with ultra-pure H_2O) was added. Samples were syringe filtered (0.45 µm MCE syringe filter (Fisher Scientific, Ottawa ON)) diluted to 20 mL with ultra-pure water and analyzed via Microwave Plasma-Atomic Emission Spectrometer (MP-AES) (4100 MP-AES; Agilent Technologies, Santa Clara, CA) at the University of Saskatchewan Soil Science Laboratory. Fe, Mg, and Mn were analyzed at wavelengths of 259.940 nm, 518.360 nm, and 257.610 nm, respectively.

2.2.4.4 Sediment physical parameters and chemistry data analysis

Correlations were run between EPC_0 by site type, and % fines (R-project, R Core Team 2013). Sediment fractions, if not normal, were log-transformed and compared to EPC_0 values (August) using a Pearson correlation. Additionally, a two-way ANOVA was run to assess differences in site type within each fraction and between metal oxide and Ca-bound P fractions

(R-Project, R Core Team 2013). Sediment metals data, if not normal, were transformed and compared to EPC_0 values using a Pearson's product moment correlation (R-Project, R Core Team 2013). Sediment fractions were compared to EPC_0 from August 2013 and by site type, stream pool or reservoir.

2.3 Results

2.3.1 Water quality and sediment parameters

The majority of measured water chemistry and physical parameters changed during the sampling season (Table A.1), with overall differences shown between the site types in five parameters (Table 2.2). Stream pools were significantly higher in Ca^{2+}, pH, dissolved oxygen, and conductivity (p=0.028, p=0.015, p=0.011, p=0.021, respectively, asymptotic Wilcoxon Mann-Whitney Rank-Sum permutation test), while reservoirs were significantly higher in organic matter in sediment (p=0.001, asymptotic Wilcoxon Mann-Whitney Rank-Sum permutation test). Median values of all water quality, physical, and phosphorus sorption parameters throughout the field season can be found in Table 2.3; all values for water quality parameters collected for each month can be found in Appendix A Table A.1.

Table 2.2 Comparison of median values for water quality and physical parameters between reservoirs and stream pools, medians over all months of the study. Asterisks denote whether median values for seasonal data within 7 pools and 8 reservoirs were significant different between reservoirs and stream pools according to an asymptotic Wilcoxon Mann-Whitney Rank Sum permutation test.

Water Quality Parameter	Reservoir	Stream pool
Soluble Reactive phosphorus (mg L^{-1})	0.209	0.117
Total phosphorus (mg L^{-1})	0.252	0.170
Ca^{2+} (mg L^{-1})	58.84*	96.96*
Mg^{2+} (mg L^{-1})	20.06	24.14
pH	7.70*	8.12*
Dissolved Oxygen (mg L^{-1})	7.7*	9.2*
Conductivity (mS m^{-1})	494.8*	686.0*
Alkalinity (mg L^{-1})	236.9	256.1
% Organic matter in sediment	2.44**	0.68**
Dissolved Organic Carbon (mg L^{-1})	9.9	8.2
% fines (Clay + silt)	71.13	59.45

*Significant at the 0.05 probability level
**Significant at the 0.01 probability level

Table 2.3 Median values of water quality and sediment parameters for each site throughout the field season. Reported values are for: equilibrium phosphorus concentration (EPC_0), soluble reactive phosphorus (SRP), total phosphorus (TP), calcium ions (Ca^{2+}), magnesium ions (Mg^{2+}), dissolved oxygen (DO), pH, conductivity, alkalinity, organic matter in sediment (OMS), dissolved organic carbon (DOC), and % fines (particle size <05mm).

Site	SRP	TP	Ca^{2+}	Mg^{2+}	DO	pH	Conductivity	Alkalinity	OMS	DOC	Fines
	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}		mS m^{-1}	mg L^{-1}	%	mg L^{-1}	%
R1	0.221	0.275	57.19	20.35	7.88	7.55	426.0	251.9	2.43	9.9	66.69
R2	0.240	0.360	47.44	17.24	6.89	7.57	421.0	206.1	2.70	9.9	75.62
R3	0.198	0.228	64.41	24.98	7.24	7.73	512.0	285.8	1.32	7.8	54.92
R4	0.178	0.221	59.26	25.11	7.62	7.57	499.0	292.5	2.39	6.5	79.57
R5	0.252	0.460	43.38	14.14	9.20	8.49	433.0	12.7	2.45	12.7	68.10
R6	0.245	0.346	58.41	19.77	6.30	7.85	490.5	241.5	2.91	12.4	68.34
R7	0.019	0.117	158.99	18.54	8.85	7.69	936.5	172.3	1.98	10.4	81.13
R8	0.013	0.045	79.20	27.36	9.03	7.91	648.5	232.3	2.72	9.8	73.83
P1	0.121	0.141	76.26	23.81	9.05	8.23	591.0	274.2	0.45	8.2	44.68
P2	0.141	0.173	65.56	20.20	9.59	8.07	522.0	239.1	0.68	8.1	59.45
P3	0.117	0.210	80.50	20.74	9.57	8.12	622.5	249.9	0.68	7.7	41.82
P4	0.122	0.139	101.82	24.14	9.00	8.26	686.0	297.8	0.50	6.8	38.35
P5	0.092	0.268	96.96	24.69	9.45	8.11	734.0	256.1	0.71	8.4	65.61
P6	0.039	0.170	120.08	56.96	9.22	8.20	1200.0	262.0	0.81	10.1	93.12
P7	0.024	0.042	134.36	57.64	8.80	7.97	1277.0	256.0	0.93	10.1	88.67

2.3.2 Range of EPC_0 values

Equilibrium phosphorus concentration values ranged from 0.005 mg P L^{-1} to 0.603 mg P L^{-1} across all sites and dates (Figure 2.2, Table 2.4). Both the highest and lowest EPC_0 values corresponded to reservoir sites. Twelve EPC_0 values were above 0.100 mg P L^{-1}. Ten of these values were divided among three different reservoirs over time, with two of these reservoirs showing sustained high values throughout the field season. Two stream pools also showed EPC_0 values in excess of this threshold late in the season (August). It is important to note that although the stream pools in this study spanned a larger geographic area, these sites actually showed less variation than reservoirs (Figure 2.2, Table 2.4).

Each site's EPC_0 values were plotted against Julian day number to make month to month comparisons at individuals sites (Figure 2.3). Five sites (R4, R6, P1, P3, and P7) showed a general pattern of decrease in EPC_0 throughout the sampling period. Other sites (R5, R7, P5 and P6) showed little change, or inconsistent patterns through time (R1, R2, R3, R8, P2, and P4). On average there was a 3.3 fold change (max value/min value) in EPC_0 values throughout the season (Figure 2.3).

For all sites, regardless of site type, EPC_0 was inversely related to the distribution coefficient, K_d (Pearson's Product Moment Correlation, r= -0.7135, p<0.0001) and the partition coefficient (Pearson's Product Moment Correlation, r= -0.767, p<0.0001). The RSP in reservoirs was significantly larger than that of streams (p=0.002, asymptotic Wilcoxon Mann-Whitney Rank Sum permutation test) while K_d and partition coefficients were not significantly different. EPC_0 values for different site types and months were compared using a one way RM-ANOVA and no significant difference was found between months or between month and site type or between site types (Table 2.5).

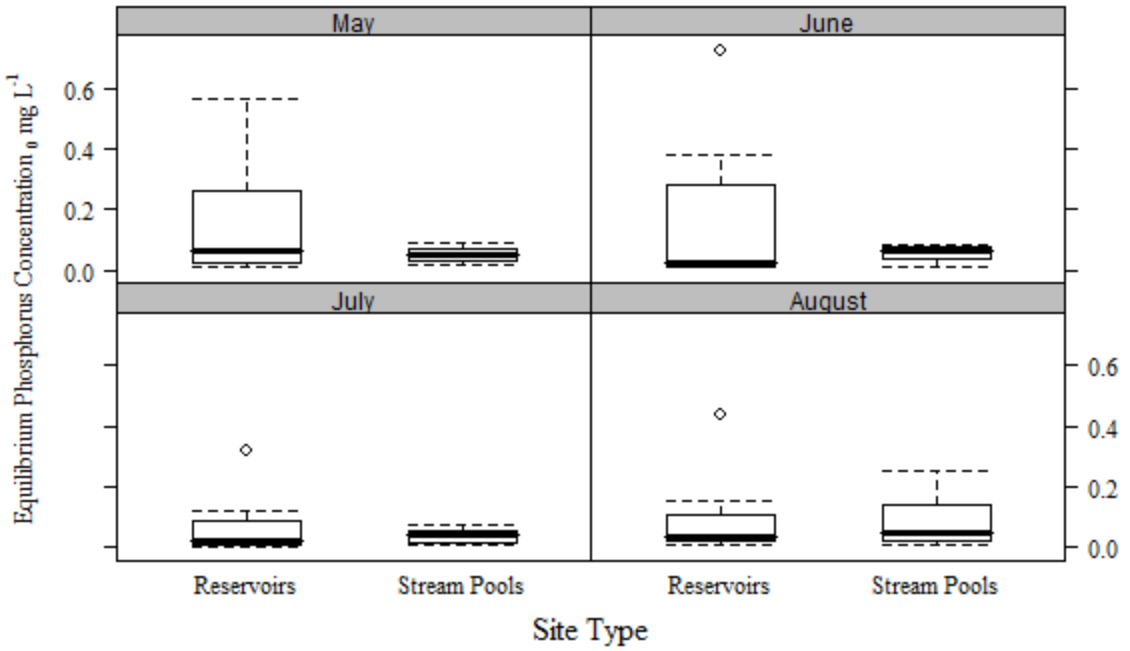

Figure 2.2 Boxplots of EPC_0 values of each month separated into site type. The bold line represents the median value, the top and bottom of the box represent the 3rd and 1st percentile, respectively, the whiskers represent Tukey's 1.5 Inter Quartile Range, and the small circles represent an outlier (outside of 1.5 x Inter Quartile)Range.

Table 2.4 Equilibrium Phosphorus Concentration (EPC_0), Soluble Reactive Phosphorus (SRP), EPC_0 Relative Saturation and coefficients derived from the initial mass isotherm Partition Coefficient (slope-unitless), Reactive Soil Pool (RSP) and distribution coefficient (K_d).

	Site	EPC_0 (mg L^{-1})	SRP (mg L^{-1})	EPC_{sat} (%)	Sink/Source	Partition Coefficient	RSP (mg kg^{-1})	$K_d \times 10^{-3}$ (L kg^{-1})
May	R1	0.281	0.153	46	Source	0.905	27.57	0.10
	R2	0.245	0.271	-11	Equilibrium[a]	0.903	16.90	0.09
	R3	0.068	0.157	-132	Sink	0.999	167.14	13.65
	R4	0.567	0.186	67	Source	0.808	22.69	0.04
	R5	0.013	0.137	-921	Sink	0.998	45.91	4.70
	R6	0.052	0.177	-237	Sink	0.989	33.78	1.00
	R7	0.023	0.029	-26	Sink	0.998	16.90	3.93
	R8	0.029	0.004	88	Source	0.999	166.57	7.54
	P1	0.065	0.144	-121	Sink	0.938	6.22	0.15
	P2	0.088	0.193	-120	Sink	0.947	13.85	0.16
	P3	0.068	0.140	-106	Sink	0.966	16.41	0.28
	P4	0.053	0.144	-173	Sink	0.971	16.84	0.32
	P5	0.014	0.129	-814	Sink	0.994	29.30	1.74
	P6	0.015	0.113	-677	Sink	0.992	19.65	1.22
	P7	0.043	0.117	-176	Sink	0.981	20.98	0.46
June	R1	0.177	0.288	-62	Sink	0.898	14.27	0.08
	R2	0.609	0.492	18	Equilibrium[a]	0.850	26.30	0.06
	R3	0.021	0.239	-1048	Sink	0.996	45.93	3.17
	R4	0.383	0.169	56	Source	0.952	75.48	0.20
	R5	0.016	0.356	-2139	Sink	0.993	23.01	1.19
	R6	0.027	0.319	-1068	Sink	0.986	18.35	0.70
	R7	0.007	0.166	-2256	Sink	0.999	29.73	7.38
	R8	0.009	0.154	-1646	Sink	0.992	15.00	1.47
	P1	0.067	0.208	-209	Sink	0.923	7.99	0.11
	P2	0.082	0.185	-126	Sink	0.950	14.65	0.18
	P3	0.065	0.169	-122	Sink	0.956	12.44	0.19
	P5	0.012	0.147	-1125	Sink	0.985	13.21	0.56
July	R1	0.119	0.373	-213	Sink	0.913	11.61	0.10
	R2	0.061	0.209	-244	Sink	0.984	49.50	0.79
	R3	0.014	0.172	-1111	Sink	0.997	40.00	3.46
	R4	0.319	0.357	-12	Equilibrium[a]	0.907	34.53	0.11
	R5	0.014	0.202	-1303	Sink	0.999	95.13	92.69
	R6	0.022	0.252	-1043	Sink	0.995	35.96	1.67
	R7	0.005	0.009	-89	Sink	0.999	41.56	8.82
	R8	0.007	0.021	-213	Sink	0.999	61.92	11.10
	P1	0.044	0.098	-121	Sink	0.938	6.49	0.14
	P2	0.075	0.098	-30	Sink	0.957	16.21	2.17
	P3	0.046	0.094	-105	Sink	0.973	16.44	0.32
	P4	0.062	0.122	-95	Sink	0.956	9.99	0.16
	P5	0.021	0.055	-158	Sink	0.993	28.47	13.44
	P6	0.014	0.010	28	Source	0.991	12.85	0.96
	P7	0.008	0.024	-199	Sink	0.996	19.24	1.78
August	R1	0.435	0.113	74	Source	0.752	20.80	0.05
	R2	0.048	0.179	-275	Sink	0.988	50.62	1.10
	R3	0.023	0.057	-153	Sink	0.996	95.42	4.78
	R4	0.153	0.171	-12	Equilibrium[a]	0.901	18.35	0.12
	R5	0.020	0.301	-1391	Sink	0.995	22.09	1.17
	R6	0.019	0.237	-1125	Sink	0.995	28.08	1.89
	R7	0.007	0.003	64	Source	0.999	62.50	12.04
	R8	0.061	0.005	92	Source	0.998	90.26	11.77
	P1	0.046	0.060	-31	Sink	0.962	10.40	0.23
	P2	0.254	0.095	62	Source	0.973	87.73	0.35
	P3	0.047	0.086	-80	Sink	0.979	20.70	0.42
	P4	0.236	0.097	59	Source	0.955	36.73	0.15
	P5	0.023	0.038	-63	Sink	0.988	16.71	0.67
	P6	0.013	0.039	-188	Sink	0.993	19.43	1.16
	P7	0.028	0.017	38	Source	0.997	16.11	2.54

[a] Equilibrium where relative EPC_{sat} is between +20% and -20% (Jarvie et al 2005).

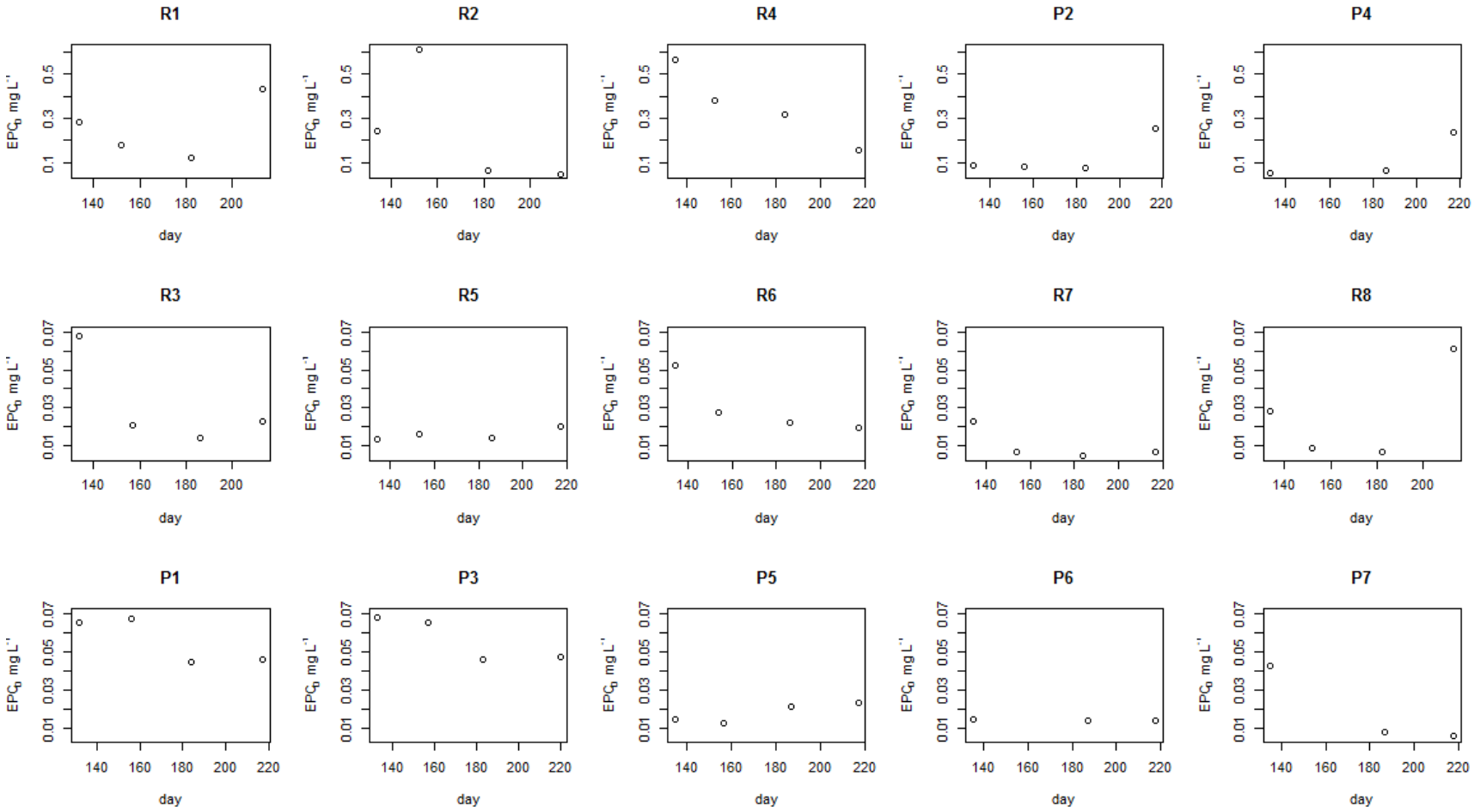

Figure 2.3 Multiplot of Equilibrium Phosphorus Concentration (EPC_0) mg L^{-1} against day number for each site throughout the field season. The top row (R1, R2, R4, P2, and P4) consisted of higher EPC_0 values and are plotted on a y-axis scale (0.07-0.61), the second and third rows are lower and are plotted on a y-axis scale (0.005-0.07).

Table 2.5 Results from repeated measures ANOVA testing whether equilibrium phosphorus concentrations vary by month or site-type (reservoir vs stream pool).

ANOVA	Effect	d.f.	F statistic	*p* value
Repeated measures	Month	3	1.302	0.285
	Site Type	1	2.687	0.108
	Month x Site Type	3	0.485	0.694

* Significant at the 0.05 probability level

2.3.3 Range of EPC_0 Relative saturation values

There was high variability in the relative saturation of equilibrium phosphorus concentrations (Figure 2.4) which ranged from -2256% to 92% relative saturation. No significant difference in relative saturation was observed across months (non-parametric Kruskal-Wallis test; p=0.2809). Median of EPC % saturation values are in Table 2.4.

Eleven measurements were below -1000% relative saturation, with ten of these measurements in 5 separate reservoirs (R3, R5, R6, R7, and R8) and one stream pool (P5). These extremely low values were spread throughout the field season (six measurements in June (R3, R5, R6, R7, R8, P5), three in July (R3, R5, R6), and two in August (R5, R6)). Eleven measured values were above 20% relative saturation during the duration of the sampling period with seven values occurring in four separate reservoirs and three values in separate stream pools (three May, one in June, one in July, and six in August). Four samples throughout the study period, which came from two separate reservoirs, showed values near equilibrium (Table 2.4; defined as ± 20%; Jarvie et al 2005).

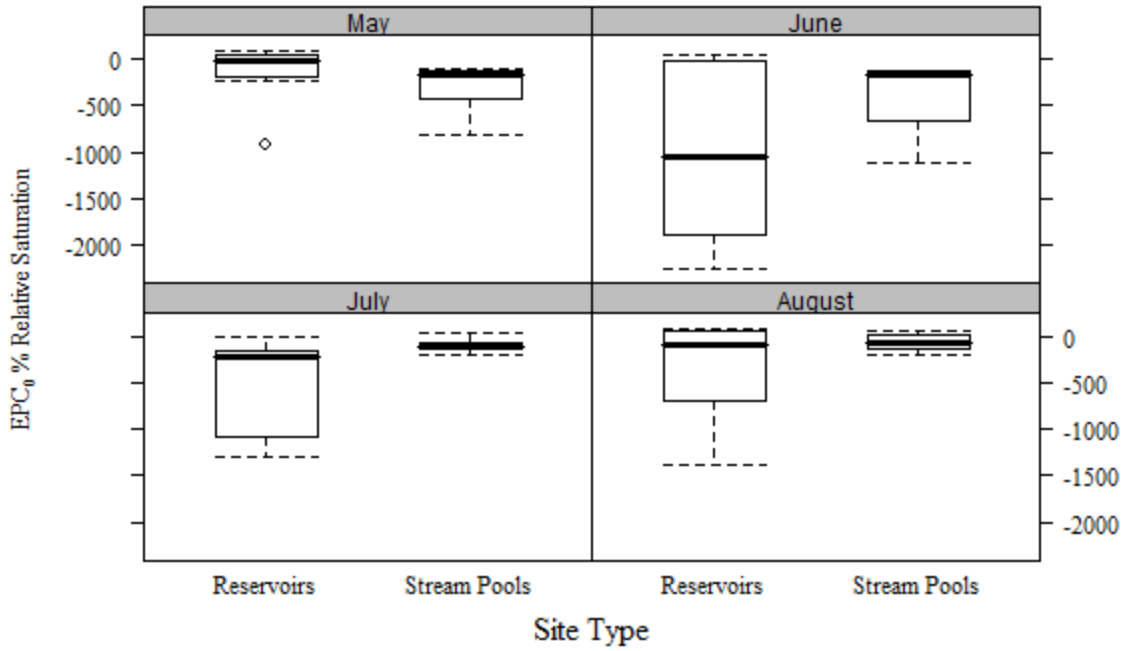

Figure 2.4 Boxplots of EPC_0 Relative Saturation values of each month seperated into site type. The bold line represents the median value, the top and bottom of the box represent the 3rd and 1st percentile, respectively, the whiskers represent Tukey's 1.5 Inter Quartile Range, and the small circle represents an outlier (outside of 1.5 x Inter Quartile)Range.

2.3.4 Sediment fractionation and metals in sediment

The largest measured P fraction was the metal oxide bound fraction (12-14% of total P determined through fractionation; stream pools and reservoirs, respectively). Ca-bound P fraction (also includes Mg-bound P) accounted for 2-4% of total P (stream pools and reservoirs). None of the phosphorus fractions differed significantly between site types (Table 2.6). Metal oxide bound P median concentrations were significantly higher (0.093 mg P g^{-1} and 0.081 mg P g^{-1} for reservoirs and stream pools respectively) than Ca-bound P median concentrations (0.027 mg P g^{-1} and 0.015 mg P g^{-1} for reservoirs and stream pools respectively) across the site types (Tables 2.6, 2.7; post-hoc Tukey $p<0.0001$). A large proportion of sediment total P was not accounted for in these two fractions and could be attributed to organic P. A summary of average values for individual site metal oxide P, Ca-bound P, and total P in sediments can be found in Table 2.8. Iron made up the largest portion of metals in sediments at 1.5% in reservoirs and 1.9% in streams. Magnesium and manganese made up smaller fractions with Mg making up 0.5% in reservoirs and 0.7% in streams, while Mn made up 0.1% in reservoirs and 0.3% in streams.

Pearson's product moment correlations were run in order to assess relationships between metals found in sediment, P fractions, and EPC_0 values in August, the month for which detailed sediment analyses were performed. Mn was significantly related to EPC_0 in both reservoirs and stream pools (Table 2.9), although the direction of the relationship differed. Individual metals were compared between site types and a significant difference was observed, with higher Mn in stream pool sediments (p= 0.036, two-sample t-test; Table 2.10).

Table 2.6 P fractions median values of reservoir and ponding stream sediments. Reservoir n=8, ponding stream n=7 per site type. *p* value from a three way ANOVA assessing differences between stream pool and reservoir sites for each fraction

Site	Metal Oxide-bound P[†]	Ca-bound P[†]	Total P
	(mg of P g^{-1} oven dried sediment)		
Reservoir	0.093	0.027	0.677
Stream Pool	0.081	0.015	0.676
P	0.999	0.399	0.999

[†] Geometric mean and 95% CI back-transformed from $\log_{10}$ transformation.

Table 2.7 Results from three way between groups ANOVA testing for differences between fraction type P concentrations (metal oxide bound-P, Ca-bound P, and total P) and for differences of site type within fraction type.

ANOVA	Effect	d.f.	F statistic	*p* value
Three way between groups ANOVA	Fraction Type	2	139.91	<0.001
	Site type	1	1.670	0.204
	Fraction type x Site type	2	1.057	0.357

Table 2.8 Average ± standard deviation (mg P g^{-1}) of phosphorus bound to metal oxides (P-Metal Oxide), phosphorus bound to calcium (P-calcium) and total phosphorus bound to sediment.

	P-Metal Oxide	P-calcium	Total Phosphorus
	(mg P g^{-1} oven dried sediment)		
R1	0.093 ± 0.010	0.029 ± 0.003	0.825 ± 0.054
R2	0.085 ± 0.004	0.104 ± 0.003	0.523 ± 0.040
R3	0.096 ± 0.007	0.035 ± 0.003	0.265 ± 0.023
R4	0.108 ± 0.003	0.010 ± 0.001	0.573 ± 0.083
R5	0.134 ± 0.006	0.007 ± 0.001	0.435 ± 0.014
R6	0.126 ± 0.005	0.024 ± 0.003	0.783 ± 0.067
R7	0.078 ± 0.007	0.015 ± 0.001	0.780 ± 0.091
R8	0.012 ± 0.002	0.061 ± 0.009	1.106 ± 0.034
P1	0.079 ± 0.001	0.005 ± 0.001	0.270 ± 0.033
P2	0.098 ± 0.002	0.027 ± 0.005	0.676 ± 0.067
P3	0.151 ± 0.002	0.018 ± 0.002	1.263 ± 0.097
P4	0.064 ± 0.005	0.011 ± 0.001	0.913 ± 0.110
P5	0.081 ± 0.006	0.014 ± 0.001	0.242 ± 0.026
P6	0.103 ± 0.010	0.023 ± 0.001	0.817 ± 0.003
P7	0.068 ± 0.003	0.015 ± 0.001	0.604 ± 0.085

Table 2.9 Pearson's product moment correlation coefficients (*r)* of relationship between sediment fractions and metals bound to sediment with EPC_0. EPC_0 and Calcium bound P data were natural log transformed, metal oxide bound P was transformed by taking the inverse, Mg was transformed by taking the inverse and Mn was square root transformed.

	August	August Reservoirs	August stream pools
	r	*r*	*r*
Calcium- P	0.10	0.17	0.01
Metal Oxide-P	-0.01	-0.10	0.04
Total P	0.22	0.22	0.23
Fe	-0.40	-0.28	-0.67
Mg	0.17	-0.35	0.65
Mn	-0.02	-0.84†	0.74†

†Significant relationship at p =0.05

Table 2.10 Metals bound to sediment [mean (95% CI) of reservoir and ponding stream sediments. Reservoir n=8, stream pool n=7]. *P* values from two sample t-test between reservoirs and stream pools for each metal.

Site	Fe	Mg	Mn
	(g of metal kg^{-1} oven dried sediment)		
Reservoir	14.54	4.69	1.18
	(11.03-18.05)	(3.22-6.16)	(0.42-1.94)
Stream pool	18.70	7.47	2.71
	(15.95-21.45)	(4.41-10.53)	(1.39-4.01)
p	0.074	0.141	0.036†

†Significant difference at p =0.05

2.3.5 Correlations with EPC_0 and between parameters

2.3.5.1 Particle size analysis and water quality parameters

A significant negative correlation (Pearson's Product Moment Correlation, r = -0.678, p=0.0002) was observed between EPC_0 and the % fines portion (< 0.05 µm) of the sediment within stream pools explaining 46% of the variability (Table 2.11). However, no significant relationship was observed between % fines and EPC_0 in the reservoirs. EPC_0 values showed a significant positive correlation with SRP, explaining up to 34% of the variation (Table 2.11). DOC was negatively related to EPC_0 across reservoirs and stream pools, as was conductivity and Ca^{2+}, while Mg^{2+} showed a negative relationship to EPC_0 only in stream pools (Table 2.11).

Alkalinity was significantly correlated with Ca^{2+} in all sites (Pearson's Product Moment Correlation, r = 0.524, p<0.0001) and in reservoirs and stream pools (Pearson's Product Moment Correlation, r = 0.439, p=0.012, r = 0.595, p = 0.002), respectively. Ca^{2+} was also significantly correlated with Mg^{2+} in all sites, reservoirs, and stream pools (Pearson's Product Moment

Correlation, $r = 0.716$, $r = 0.604$, $r = 0.840$, $p<0.001$). Organic matter in sediment was significantly correlated to % fines in stream pools and all sites (Pearson's Product Moment Correlation, $r = 0.659$, $p <0.001$, $r = 0.376$, $p= 0.004$), however, no relationship was observed in reservoirs.

Table 2.11 Pearson's Product Moment Correlation Coefficients (r) assessing relationship between water quality parameters and EPC_0. Asterisks indicate significance.

	All sites	Reservoirs	Stream Pools
Soluble Reactive P	0.454***	0.421*	0.579**
Total P	0.170	0.389	-0.041
Alkalinity	0.100	0.143	0.06
Dissolved organic carbon	-0.357**	-0.360*	-0.532**
% Fines	0.169	-0.183	-0.678***
Organic Matter in sediment	0.159	0.279	-0.479*
pH	-0.118	-0.148	0.152
DO	-0.039	-0.061	0.2167
Ca^{2+}	-0.472***	-0.461**	-0.579**
Mg^{2+}	-0.235	0.006	-0.674***
Conductivity	-0.506***	-0.460*	-0.695***

*Significant $p < 0.05$
** Significant $p < 0.01$
*** Significant $p < 0.001$

2.3.5.2 Best subset regression

Best subset regression was run to determine which combination of water quality and physical parameters were the best predictors of EPC_0 values. We ran best subset regression analysis with SRP as a parameter and without. In all but one set of candidate models (all sites with SRP as a parameter) the same sets of parameters were predicted (Ca^{2+}, alkalinity, organic matter in sediment (OMS), and dissolved organic carbon (DOC)).

Candidate models, with SRP as a parameter, (Table 2.12) all identified Ca^{2+} and DOC as predictors, and all but two (best model for reservoirs and stream pools) identified SRP. Alkalinity, OMS, and Mg^{2+} also appeared in different models. Candidate models, without SRP as a parameter, (Table 2.13) all identified $Ca^{2+}$and DOC as predictors. Organic matter in sediment, Mg^{2+}, pH, and DO also appeared in different models.

Each of the best models without SRP as a parameter (determined by maximized r^2 and Mallows C_p, as well as minimized S) included Ca^{2+}, DOC, and alkalinity. Similarly, models that

did not incorporate SRP all found that Ca^{2+} and DOC were the best predictors regardless of site type. The equations are reported in Table 2.14 for models using SRP and in Table 2.15 for models without SRP.

Reservoirs and stream pools had the same predictors when SRP was added to the regression analysis, Ca^{2+}, alkalinity, OMS, and DOC (Table 2.14). However when SRP was not used within the regression analysis reservoirs were best predicted by Ca^{2+}, Mg^{2+}, OMS, and DOC, while stream pools were best predicted by Ca^{2+}, OMS, DOC, and %fines (Table 2.15).

Table 2.12 Best subset Regression equations with SRP. Output values are displayed below for the three models that overall had the best fit, adjusted r^2 (adj. r^2), Mallows C_P, the square root of the mean standard error (S), the number of parameters, and the specific parameters in each model. N=57.

Reservoir	Adj. R^2	Mallows C_P	S	number of parameters	Parameters*
Model 1	0.513	2.9	0.439	4	SRP, Ca^{2+}, OMS, DOC
Model 2†	0.497	3.7	0.446	4	Ca^{2+}, alkalinity, OMS, DOC
Model 3	0.526	3.4	0.433	5	SRP, Ca^{2+}, Mg^{2+}, OMS, DOC
Stream Pool					
Model 1	0.596	2.0	0.267	4	SRP, Ca^{2+}, alkalinity, DOC
Model 2†	0.590	2.3	0.269	4	Ca^{2+}, alkalinity, OMS, DOC
Model 3	0.591	3.4	0.269	5	SRP, Ca^{2+}, DO, alkalinity, DOC
All Sites					
Model 1	0.507	3.2	0.382	5	SRP, Ca^{2+}, alkalinity, OMS, DOC
Model 2†	0.506	3.3	0.383	5	SRP, Ca^{2+}, DO, alkalinity, DOC
Model 3	0.507	4.3	0.382	6	SRP, Ca^{2+}, DO, alkalinity, OMS, DOC

† Denotes the best model for each site type based on maximized r^2 and Mallows C_p and minimized S.
*Parameters defined as Soluble Reactive Phosphorus (SRP), Calcium ions (Ca^{2+}), Dissolved Oxygen (DO), organic matter in sediment (OMS), and Dissolved Organic Carbon (DOC).

Table 2.13 Best subset regression equations without SRP. Output values are displayed below for the three models that overall had the best fit, adjusted r^2 (adj. r^2), Mallows C_P, the square root of the mean standard error (S), the number of parameters, and the specific parameters in each model. N=57.

Reservoir	Adj. r^2	Mallows C_P	S	number of Parameters	Parameters*
Model 1	0.497	2.4	0.446	4	Ca^{2+}, alkalinity, OMS, DOC
Model 2†	0.477	3.3	0.455	4	Ca^{2+}, Mg^{2+}, OMS, DOC
Model 3	0.500	3.3	0.445	5	Ca^{2+}, Mg^{2+}, OMS, DOC, pH
Stream Pool					
Model 1	0.590	1.5	0.269	4	Ca^{2+}, alkalinity, OMS, DOC
Model 2†	0.573	2.2	0.274	4	Ca^{2+}, OMS, DOC, % Fines
Model 3	0.578	3.2	0.273	5	Ca^{2+}, DO, alkalinity, OMS, DOC
All Sites					
Model 1	0.490	2.0	0.389	4	Ca^{2+}, alkalinity, DOC, pH
Model 2†	0.489	2.2	0.389	4	Ca^{2+}, alkalinity, OMS, DOC
Model 3	0.587	3.4	0.390	5	Ca^{2+}, DO, alkalinity, DOC, pH

†Denotes the best model for each site type based on maximized r^2 and Mallows C_p and minimized S.
*Parameters defined as Calcium ions (Ca^{2+}), Dissolved Oxygen (DO), organic matter in sediment (OMS), and Dissolve Organic Carbon (DOC).

Table 2.14 Best subset regression best fit model equations with SRP, R^2, number of samples (n) and the *p* values of ANOVAs. EPC_0 mg L^{-1} predicted by parameters defined as Soluble Reactive Phosphorus (SRP) mg L^{-1}, Calcium ions (Ca^{2+}) mg L^{-1}, organic matter in sediment (OMS) % of Total, and Dissolved Organic Carbon (DOC) mg L^{-1}, alkalinity mg L^{-1}, dissolved oxygen (DO) mg L^{-1}.

Site type	Resulting Equation	Adj r^2	n	*p*
Reservoir	$Log_{10}(EPC_0) = -1.94\times log_{10}[Ca^{2+}] + 0.002\times Alkalinity + 0.25\times OMS (\%) - 0.11\times DOC + 2.22$	0.497	32	<0.0001
Stream Pools	$Log_{10}(EPC_0) = -2.30\times log_{10}[Ca^{2+}] + 0.0022\times Alkalinity + 0.47\times OMS (\%) - 0.08\times DOC + 3.46$	0.590	25	<0.0001
All sites	$Log_{10}(EPC_0) = 1.02\times sqrt[SRP] - 1.53\times log[Ca^{2+}] + 0.02\times DO + 0.002\times Alkalinity - 0.10\times DOC + 1.24$	0.506	57	<0.0001

Table 2.15 Best subset regression best fit model equations without SRP, R^2, number of samples (n), and the *p* values of ANOVAs. EPC_0 mg L^{-1} predicted by parameters defined as Calcium ions (Ca^{2+}) mg L^{-1}, magnesium ions (Mg^{2+}) mg L^{-1}, Dissolved Oxygen (DO) mg L^{-1}, organic matter in sediment (OMS) % of Total, % of fines in total sediment, alkalinity mg L^{-1}, and Dissolved Organic Carbon (DOC) mg L^{-1}.

Site type	Resulting equation	Adj. r^2	n	*p*
Reservoir	$Log_{10}(EPC_0) = -2.04 \times \log[Ca^{2+}] + 0.87 \times \log[Mg^{2+}] + 0.26 \times OMS (\%) - 0.11 \times DOC + 1.71$	0.497	32	<0.0001
Stream Pools	$Log_{10}(EPC_0) = -1.76 \times \log[Ca^{2+}] - 0.71 \times OMS (\%) - 0.11 \times DOC + 0.0012 \times (\% Fines) + 4.40$	0.573	25	<0.0001
All Sites	$Log10(EPC_0) = -2.09 \times \log[Ca^{2+}] + 0.002 \times Alkalinity + 0.12 \times \log[OMS (\%)] - 0.10 \times DOC + 2.83$	0.489	57	<0.0001

2.3.6 Artificial water and stream water

To determine if artificial stream water was a suitable alternative to stream water, the EPC_0 values of artificial stream water and phosphorus-spiked stream water were log-transformed and compared. A paired t-test on transformed data showed no significant difference between the methods (α=0.05, *p*=0.633, d.f.=8). Additionally, paired t-tests run on transformed binding coefficients, K_d, RSP, and partition coefficient showed no significant difference between the methods (α=0.05, *p*=0.125, *p*=0.347, *p*=0.114, d.f.=8, respectively). However, the percent (%) variation between results of the two methods had a large range (Table 2.16) as the absolute average % variation between methods was 65% (0.062 mg L^{-1}). For context, the percent variation of replicate samples run using artificial water was 7.4% (0.007 mg L^{-1}) (Appendix A Figure A.2). Regressing the artificial water EPC_0 values against stream water EPC_0 values demonstrates a linear relationship (Figure 2.5), with an intercept of -0.034 (95% CV [-0.146-0.078]) and a slope equal to 1.134 (95% CV [0.705-1.882]).

Table 2.16 EPC_0 of the sample specific artificial water and natural stream water augmented with phosphorus (ambient stream water), difference, and % variation.

Month	Site	EPC_0 Artificial Water mg L^{-1}	EPC_0 Ambient Stream Water mg L^{-1}	Absolute Difference mg L^{-1}	% Variation
June	R4	0.383	0.543	0.160	-35
August	R1	0.435	0.387	0.048	11
	R7	0.007	0.003	0.004	73
	R8	0.061	0.020	0.041	102
	P1	0.046	0.079	0.033	-53
	P2	0.254	0.122	0.132	70
	P4	0.236	0.129	0.107	59
	P5	0.023	0.041	0.018	-55
	P7	0.028	0.012	0.016	75

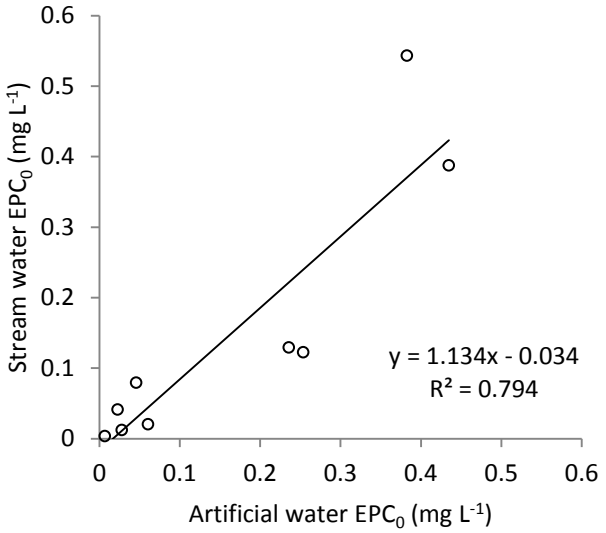

Figure 2.5 Type II regression of artificial water EPC_0 against natural stream water EPC_0 for sites R4 (June) and R1, R7, R8, P1, P2, P4, P5, P7 (August).

2.4 Discussion

2.4.1 EPC_0, environmental parameters, and nutrient dynamics

Equilibrium phosphorus concentration values provide an indication of the direction of transport for dissolved phosphorus (P) within sediments (Froelich 1988). In this study, we saw ~75% of measurements indicated potential for net P sorption from the water column. Seven of the 15 sites were consistently P sinks through the study with an eighth transitioning between equilibrium and sink conditions. In the remainder of sites (seven), data suggested a net flux of P from the sediments was occurring on at least one sampling date.

While the majority of both headwater reservoirs and stream pools exhibited similar behavior, there were identifiable water chemistry and sediment differences between the two site types. Organic matter in sediment was significantly higher in reservoirs; this is consistent with the longer residence times and the limited scouring and flushing events that allow organic matter to build up in these areas (Tiessen et al. 2011). Dissolved Ca^{2+} concentrations were significantly higher in stream pools; this may be due to the position of the stream pools at lower elevations, where there is a stronger influence of Ca^{2+} due to the Manitoba Escarpment (Michalyna et al. 1988). Similarly, conductivity was also higher in stream pools, in part due to higher measured Ca^{2+} concentrations (Kalff 2003). Dissolved oxygen was significantly higher in stream pools, likely in part due to the continuous flow that was exhibited throughout the latter part of the season in five out of seven stream pools while reservoirs received zero flow at this time. Significantly higher pH values were observed in stream pools consistent with the increased Ca^{2+} concentrations and higher DO concentrations. Higher values of DO and pH can favor P binding to both metal oxides (related to DO; Correll 1998, White et al. 2008, Erickson et al. 2012, Sundby et al. 1986) and to calcium and magnesium compounds within the sediment (binding related to high pH; Diaz et al. 1994).

2.4.2 EPC_0 and phosphorus dynamics

Phosphorus adsorption across the Tobacco Creek Watershed exhibited a wide range of temporal variability throughout the season with a mean 3.3-fold change (max value/min value). The reservoirs had on average a 4.6-fold change while the average change was 2.0-fold in stream pools. Large variability has been seen in previous studies. The average 3.3 fold change observed in Tobacco Creek was comparable to two separate agriculturally influenced watersheds in the United Kingdom (Jarvie et al. 2005). The Avon (1650 km^2; n=8) exhibited a 2.6 fold change

while the Wye (4136 km^2; n=7) exhibited an average 3.9 fold change (Jarvie et al. 2005). Tobacco Creek exhibited more variability than the 1.4 fold change found in Illinois streams (McDaniel et al. 2009) or the 1.2 fold change in a mixed land use river system in north-east Scotland (Stutter and Lumsdom 2008). However, the variability exhibited in these agriculturally influenced streams is much lower than that observed in shaded streams in central New York State (USA) wooded areas, where EPC_0 showed a 6.4 fold change (Klotz 1991).

Despite the large variability, reservoirs and their natural analog stream pools share similar sink/source dynamics with upwards of 75% of reservoirs and 84% of stream pools acting as sinks of phosphorus throughout the season. 75% of partition coefficients, for all sites, were above 0.95 (theoretical max value 1) suggesting that the majority of the sites regardless of site type had a great affinity for added SRP in the system, consistent with the same majority acting as sinks. These partition coefficient values are notably high, with published partition coefficient numbers for the same 75% ranging from 0.80 in similar agricultural streams in Illinois (McDaniel et al. 2009) to 0.99 in non-impacted New Hampshire forested soils (Nodvin et al. 1986). Reservoirs had a significantly larger RSP (more P present in the sediment that can be readily released) when compared to stream pool median values. This larger reactive portion of P in the sediment may contribute to the large variability seen between reservoirs. Median RSP values in our study, regardless of site type (22.6 mg kg^{-1}), are higher than published median values in a separate agricultural stream in Illinois (10.6 mg kg^{-1}; McDaniel et al. 2009), suggesting the potential for more P release in the present study. Both site types seem to exhibit similar P sink/source behavior however individual correlations with water quality and physical parameters indicate that the variability in reservoirs may mask the parameters significantly influencing EPC_0 and P sorption coefficients.

Analogous with EPC_0 values, relative EPC_{sat} values did not show consistent seasonal trends, but continued to show high variability between months and site types (Figure 2.4). Sites with the most potential to take up additional P (very low EPC_{sat} values), did not necessarily match those sites that had the strongest tendency to sorb P (partition coefficients near one) or those sites that had a high sediment affinity for P (K_d). This is simply because those sites with strong tendencies to sorb P or have a high affinity for P have already begun to sorb P. These sites will be at various stages of P uptake and may not always correspond to those sites with potential

for more P uptake. This was also seen in a study conducted in agricultural sub-catchments to the Hampshire Avon and the Herefordshire Wye Rivers (Jarvie et al. 2005).

Calcium ions, alkalinity, DOC, and OMS were all important predictors of EPC_0 (best subset regression) regardless of whether SRP was a parameter. Both Ca^{2+} and DOC were significantly correlated in reservoirs and stream pools (Table 2.11) with more variability accounted for in stream pools. SRP concentrations in overlying water exhibit control over P released from the sediment (Jarvie et al. 2005), which may suggest an influence of SRP dynamics. This is reflected by the significant positive correlation between SRP and EPC_0 (Table 2.11) although it was selected only in one best subset regression model (incorporating all site data; Table 2.14).

Calcium ions were a predictor of EPC_0 in every best subset regression model and were significantly negatively correlated in both site types (Table 2.11). The importance of Ca^{2+} concentrations has been documented in regards to EPC_0 methodology (Nair et al. 1984) with Ca^{2+} concentrations having important influence on Ca-P mineral precipitation (Klotz 1991). In general, it has been seen that higher concentrations of Ca^{2+} (>50 mg L^{-1}) are effective in reducing solubility of Ca-P minerals (Diaz et al. 1994). Median Ca^{2+} concentrations in both reservoirs and stream pools were higher than 50 mg L^{-1}, indicating increased Ca-P mineral precipitation. Higher concentrations of Ca^{2+} observed throughout the watershed are consistent with increased Ca-P binding and additional binding sites by increased ionic concentrations. However, ten measurements, clustered in May and June, had lower Ca^{2+} concentrations (<50 mg L^{-1}); lower concentrations can influence P release from sediments (Klotz 1991, Stutter and Lumsdom 2008). These influences lead to Ca^{2+} being an important predictor of EPC_0.

Magnesium ions can also provide ionic control and influence (Lottig and Stanley 2007); however Mg^{2+} only appeared in one best subset regression model (reservoirs, without SRP as a predictor) and was only significantly correlated to EPC_0 in stream pools. Similar to alkalinity, Mg^{2+} ions were strongly correlated with Ca^{2+} ions. This relationship may have masked additional influences that Mg^{2+} had on EPC_0 in separate models.

Alkalinity is influenced by rock and soils that the stream flows through and can influence P binding in streams (Grobbelaar and House 1995). Alkalinity was correlated with Ca^{2+} concentrations; however it did not correlate to EPC_0 concentrations. Median alkalinity measures were higher in stream pools than reservoirs, consistent with the higher Ca^{2+} concentrations

recorded in stream pools. pH values >8.0 encourage Ca-P precipitation (Diaz et al. 1994), potentially having an influence on P sorption in the current study.

Dissolved organic carbon was a predictor in every best subset regression model. Our data indicate an inverse relationship between EPC_0 and DOC. It has been suggested that functional groups making up DOC compete for goethite binding areas with P (Antelo et al. 2007); however, Borggaard et al. (2004) have strongly debated that DOC has limited influences on P adsorption when exposed to aluminum and iron oxides. Others have argued the importance of DOC as a chelating agent that may complex with Fe and P, removing P from the water column in oxygenated waters (Maranger and Pullin 2003). Stutter and Lumsdom (2008) reported a 3-6x increase in SRP release when Ca^{2+} concentrations were at 40 mg L^{-1} and DOC (as fulvic acid) was increased from 2 to 20 mg L^{-1}. DOC is analyzed as a bulk mix but contains compounds with extremely variable chemistry (McDowell and Likens 1988); it is possible that the dominant forms of DOC in our study enhanced P removal from the water column. Despite the debated relationship DOC is an important predictor of EPC_0 in Tobacco Creek.

Organic matter in sediment was also a common predictor of EPC_0. In our study, OMS was significantly negatively correlated with EPC_0, consistent with the results of previous studies (Klotz 1988, Klotz 1991, McDaniel et al. 2009). P release due to the breakdown of OMS may be a parameter linked to increases in EPC_0 (Klotz, 1991). Similar to OMS, the % fines portion of sediment was also significantly correlated to EPC_0. It has been clearly shown that P has a higher affinity to bind to silt and clay (fines) particles than it does to sand due to increased availability of binding locations and higher surface area (McDowell and Sharpley, 2003, Huijun et al. 2010). This is consistent with our observed negative correlations between EPC_0 concentrations and % fines in sediments. The % fines in sediments exhibits an important influence on P sorption as it provides positively charged particles with increased surface area that influences the rapid first stage of P sorption (Froelich 1988). Organic matter in sediment and % fines were significantly correlated and may explain why the % fines portion of sediment only appeared in one model while OMS appeared in four models. The correlation between these two parameters may be covering the influences each individual parameter had on predicting EPC_0.

Dissolved oxygen (DO), an important water quality parameter, may play a role in P sorption (House and Denison 2000). However, it is not significantly correlated with EPC_0 in our data and only appears in one best subset regression model. This relationship could be obscured

by our reliance on point measurements of DO which is highly dynamic on short timescales. Dissolved oxygen influences P binding to redox sensitive metal oxides which make up 12-14% of the P found in sediment within Tobacco Creek.

Conductivity, an aggregate measure of electrical conductance in the water including influences from Ca^{2+} and Mg^{2+}, was significantly correlated to EPC_0 however; it did not appear in any of the best subset models. This may be due to the significant correlation between conductivity and both Ca^{2+} and Mg^{2+}. It is expected that as concentrations of both Ca^{2+} and Mg^{2+} increase so would the electrical conductance of the water (Tiwari et al. 2010). Therefore it is likely that the relationship seen between EPC_0 and conductivity may be significantly influenced by the relationship seen between Ca^{2+}, Mg^{2+}, and EPC_0.

2.4.3 Major pools of P: vulnerability to pH and O_2

Like many water quality and physical parameters, metals, particularly Fe, Mn, Ca^{2+}, and Mg^{2+} all influence P uptake and release through redox or pH sensitive reactions. Significantly more Mn was observed in stream pools than in reservoir sediment and a separate notable difference was observed in Fe (Table 2.6). In reservoirs, EPC_0 was negatively correlated with Mn in sediment. This relationship is expected, as additional metals would provide supplementary P binding sites, driving EPC_0 values down (House et al. 2000, Palmer-Felgate et al. 2009). However, a positive correlation was found in stream pools, which differs from expectations. It is important to note metals were only measured during the last sampling trip, therefore temporal differences in metals relating to EPC_0 are not accounted for, and may be important, particularly in high productivity periods, where low nighttime dissolved oxygen may be observed (Golterman 2001; White et al. 2008).

Metal oxide bound P, primarily made up of Fe hydroxides (Golterman 2004), is sensitive to changes in water column DO. In oxygenated waters, P sorbs to Fe hydroxides forming strong bonds over a long period of time. These strong bonds are sensitive to changes in DO when anoxic levels are reached. Median DO levels in our study do not reflect anoxic conditions; as noted, point measurements of DO are unlikely to capture DO minima.

Unlike the metal oxide bound-P, the Ca-bound P fraction may be sensitive to changes in pH values. pH values above 7.5 have been shown to facilitate Ca-P and Mg-P binding and precipitation out of the water column while values below 6.5 facilitate P release from these compounds (Golterman 2001). Median pH values in our study in both site types were above the

7.5 threshold, indicating that Ca-P and Mg- P were likely precipitating out of solution. However, like DO point measurements, point measurements of pH are also highly variable; therefore it is not possible to be certain if dissolution of precipitates due to low pH is occurring on different timescales. Calcium ions have an additional role in the precipitation of Ca-bound P fraction. Calcium ions in this study exhibited large variability with an average 40.6 mg L^{-1} spatial variation over the sampling dates. As already discussed, previous work has shown that Ca^{2+} concentrations higher than 50 mg L^{-1} increase Ca-P precipitation (Diaz et al. 1994); this is consistent with what is known about higher ionic strength increasing P sorption (Nair et al. 1984). This relationship is enhanced when pH values > 8.0 (Diaz et al. 1994). Enhanced precipitation influenced by pH values > 8.0 is likely to have only occurred in stream pools (pH 8.12, Ca^{2+} 96.96 mg L^{-1} Table 2.2).

Increased pH also introduces hydroxyl ions which compete with phosphorus for binding sites (Lijklema 1980). In our study, pH was not significantly correlated with EPC_0 concentrations, this may be indicative of the small portion of Ca-bound P that was found within the sediment. Our findings are similar to a separate study; Huang et al (2013) found that in one study site P sorption decreased with increasing pH. However, in their second study site the opposite relationship was observed, suggesting spatial heterogeneity in the dominant mechanisms driving P sorption, likely linked to differences in Ca-bound P between sites.

2.4.4 Insights and limitations from EPC_0-based approaches

EPC_0 results from experiments using artificial water with site specific Ca^{2+} and Mg^{2+} concentrations showed a strong correlation with determinations made with natural stream water, consistent with similar work in Florida wetlands (Dunne et al. 2006). The 95% CI of the slope bracketed the value of one and a 95% CI of the intercept that bracketed the value of zero. Although these results suggest that standard methods for determination of EPC_0 using artificial stream water are a good surrogate for EPC_0 using the natural water matrix, the slope of 1.13 (Figure 2.5) suggests a possible bias. The artificial water matrix may contribute to overestimation of EPC_0 values as evidenced by the large differences between EPC_0 determinations using the two types of water matrices (102% percent variation; August R8; with an absolute difference of 0.041 mg L^{-1}). Our results showing strong relationships between EPC_0 and Ca^{2+} and in some cases Mg^{2+}, combined with the large degree of spatial and temporal

variation in the concentration of these ions indicate that standardized methods using a single water matrix are unlikely to represent field-based EPC_0 values.

Despite the generally strong relationship between the methods, there were cases where large differences between EPC_0 determinations using the two types of water matrices were apparent. As previously mentioned, DOC may be a competitor of P for binding areas, but this role has been subject to debate (Borggaard et al 2004; Antelo et al. 2007; Stutter and Lumsdom 2008). If DOC is a competitor, this suggests that the S_w EPC_0 experiment had more competitors for binding sites than the A_w EPC_0 that only corrected for ionic concentration. A similar overestimation of EPC_0 values was seen in Bolster and Sistani (2009) where organic P in a dairy manure:soil solution was compared with an inorganic phosphate salt:$CaCl_2$:soil solution. The dairy manure:soil solution had high DOC content coupled with low pH values and produced lower P sorption than the inorganic phosphate salt:$CaCl_2$:soil solution used in their experiments (Bolster and Sistani 2009). Stutter and Lumsdom (2008) report increases in SRP release when increasing DOC (as fulvic acid) concentrations. DOC is a parameter influencing EPC_0 that has yet to be widely controlled for in an A_w incubation solution.

It is important to note that EPC_0 determined within the laboratory is an *ex situ* experiment with controlled parameters used to standardize the method. When this standardization is followed, it allows for comparisons between experiments (e.g., use of a standard Ca^{2+}, Mg^{2+} concentration across studies; Nair et al. 1984), however the results are not necessarily indicative of the natural system. EPC_0 concentrations under *in situ* conditions would be influenced by water chemistry and sediment physical-chemical characteristics. EPC_0 has been documented to increase as sediments become anoxic (Reddy et al. 1998; House and Denison 2000). During anoxic conditions Fe compounds can be altered to amorphous forms of Fe with the potential to sorb more P, however the bonds formed with the amorphous Fe are not as strong as those Fe compounds that form under oxic conditions, increasing EPC_0 values (Reddy and Delaune 2008). External pulses of SRP into the system also have the potential to increase EPC_0 (Ekka et al. 2006). Conversely, EPC_0 values have been shown to decrease with the addition of alum ($Al_2(SO_4)_3$) and $CaCO_3$, potentially through co-precipitation (Haggard et al 2004).

Many *ex situ* methods of laboratory EPC_0 analysis, including the current study, use microbial inhibitors to decrease the effect of biological processes (Nair et al. 1984, Lottig and Stanley 2007), with evidence suggesting that these biological processes are most important in

areas where gravel and larger particles were the dominant sediment fraction (Lottig and Stanley 2007). The soil:solution ratio used to determine EPC_0 concentrations is arbitrary, however, this ratio has a large impact on EPC_0. Previous studies on soil:solution ratios found that 1:2 ratio consistently had the highest EPC_0 values while the 1:100 ratio had the lowest EPC_0 values (Bhadha et al. 2012). In the same study there was an 84% change in EPC_0 values between the 1:2 and 1:20 ratios (Bhadha et al. 2012). Although there may be no single 'best' method for EPC_0 determination (Bhadha et al. 2012), where understanding the natural environment is the major goal, experiments should be conducted to best match natural conditions and care should be taken when using EPC_0 concentrations to inform management decisions based on the numerous ways EPC_0 experiments can be conducted, and evidence of the short timescale upon which EPC_0 can change.

2.5 Conclusions

This work is important in the understanding P retention in head water reservoirs and downstream pools. Results show that sediments have a high capacity for P retention, which is expected to be maximized by increased residence time of these quiescent habitats. EPC_0 values in stream pools and EPC_0 values in headwater reservoirs were not significantly different, and instead, a very high degree of temporal and spatial variability in EPC_0 was observed across the watershed, which is likely due to substantial variation in water chemistry, sediment, and sorption (RSP) characteristics that influence EPC_0. This level of variation and the physical influences of the escarpment creates substantive challenges in watershed modelling where, particularly at low-flow, EPC_0 is an influential parameter affecting P concentrations (Lepistö et al. 2014).

Through best subset regression Ca^{2+}, dissolved organic carbon, alkalinity, and organic matter in sediment were all identified as important parameters for predicting EPC_0, consistent with relationships found in previous studies (Nair et al. 1984, Bolster and Sistani 2009, McDaniel et al. 2009). Univariate correlation analyses also showed strong negative correlations between EPC_0 and % total fines and EPC_0 and Mg^{2+} in stream pools, consistent with the additional binding areas that Mg^{2+} and fine sediments provide (McDaniel et al. 2009). Dissolved organic carbon had a negative relationship with EPC_0 indicating that DOC may have been driving down the EPC_0 value. Ca^{2+} and conductivity had a negative relationship with EPC_0 in both streams and reservoirs. The negative relationship with Ca^{2+} is consistent with supplementary binding areas for P and increased Ca-P precipitation driving EPC_0 values down (Nair et al. 1984, Diaz et al. 1994). Although reservoirs and stream pools share similar dynamics and EPC_0 predictors, the large amount of variability exhibited in reservoirs suggest that local controls of chemistry and sediments may be more important than the physical distinction between naturally occurring stream pools and constructed reservoirs.

It is not possible to control for all external factors when determining EPC_0. Site by site variation was of increasing concern in the small (~1000 km^2) agriculturally dominated watershed, where Ca^{2+}, Mg^{2+}, and DOC concentrations exhibited 2.1, 4.3, and 1.3 fold differences in space at a single time point. We chose to control for Ca^{2+} and Mg^{2+} ions in our artificial water mixes, but also ran EPC_0 with collected stream water. We found that controlling for site specific Ca^{2+} and Mg^{2+} concentrations was a suitable alternative to running EPC_0 with collected stream water; however if possible (i.e., where $SRP<EPC_0$) EPC_0 should be run on

collected stream water due to the apparent importance of DOC and potential for other, uncontrolled solutes to affect EPC_0. The importance of ionic control has been well established and was corroborated by best subset regression analysis in this study. Since Ca^{2+} had a consistent influence on EPC_0 values, it should be controlled for in future batch sorption experiments in order to determine ecologically relevant sorption values, not laboratory inflated EPC_0 values.

Reduction of nutrient loads in snowmelt dominated regions is a challenge, due to the large proportion of runoff, and nutrient export that occurs at this time. Flashy runoff events in the catchment (Corriveau et al. 2011), combined with recent large rain events (Tiessen et al. 2011) lead to rapid flushing of dissolved nutrients, and provide limited time for nutrient interactions with the sediment. As a result, although most sediments in the slower-flow areas of the catchment (pools, reservoirs) have the capacity to sorb P, the greatest effect is likely to be on concentrations at low flow, with a lesser effect on overall downstream nutrient export during major snowmelt and rainfall runoff events. Headwater dams, such as those in Tobacco Creek, are useful BMPs for storage and reducing peak flow (Tiessen et al. 2011). Reduced flow and an increase in residence time help to increase sediment-water interactions in both reservoirs and stream pools, which is likely to help reduce P export due to the tendency for sediments to sorb P. What is not known is the permanence of P retention, in terms of sensitivity to release at low DO, and with fluctuating pH. Our data indicate that release at low DO would have a greater impact due to the size of the DO sensitive P pool, while pH sensitive species remain rare. This work shows clear evidence of a tendency for sorption of P by sediments from ~2 weeks after peak snow melt to late summer, and indicates that constructed dams do not differ significantly from their natural analog of stream pools in their tendency to sorb P.

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CHAPTER 3: ASSESSMENT OF DIEL NUTRIENT DYNAMICS IN SMALL HEADWATER RESERVOIRS USING HIGH FREQUENCY PHOSPHORUS SENSORS

To date, few studies have examined diel (daily) changes in phosphorus (P) chemistry in aquatic ecosystems, despite the potential for key drivers of P chemistry to change on short timescales. The purpose of this chapter is to 1) assess the reliability of high frequency automated sensors as a tool to understand changes in P concentrations, 2) determine if diel changes in P concentrations were observable in a series of agricultural impoundments, and 3) identify conditions associated with diel variation. We found that data derived from *in situ* high frequency automated sensors was correlated with results of traditional sampling and analytical approaches (r^2 = 0.654-0.963). Consistent diel changes in P concentrations were only observed in late summer (August) and variations between average maximum and minimum SRP values ranged from 41-64%. The timing of diel cycles varied between reservoirs and sensor deployment depths. Future water quality monitoring regimes should aim to sample phosphorus in the mid-morning hours to avoid over or underestimation of P concentrations in the water column.

3.1 Introduction

Variation in water quality occurs on yearly, seasonal, event, and diel time scales (Dahlgren et al. 2004). Typical sampling frequency (daily, weekly, monthly) fails to account for diel changes, and can introduce systematic bias into monitoring programs (Baulch et al. 2012). In addition, it may obscure potentially important information about ecosystem processes. Although there has been limited research assessing diel (daily) cycles in phosphorus concentrations, there are numerous reasons to anticipate that diel changes in concentrations may occur. Photosynthetic organisms preferentially assimilate nutrients such as P and nitrogen during daylight hours (Raven and Geider 1988). This process may work to depress P levels during daylight hours (Figure 3.1). Geochemical factors are also likely to be important. Remobilization of P stored in streambed sediments is affected by changes in environmental conditions, which in turn are linked to ecological metabolism (Bäckström et al. 2002, Mulholland et al. 2005, Forget et al. 2008, Nimick et al. 2011, Cohen et al. 2013). It has been hypothesized that diel variation in P is related to significant changes in pH and dissolved oxygen (DO) (Grobbelaar and House 1995, Golterman 2004, Lukkari et al. 2007). Dissolved oxygen decreases at night, due to ecosystem respiration in the absence of significant photosynthesis. pH shows contrasting patterns, driven by CO_2 drawdown in daytime and increases at night.

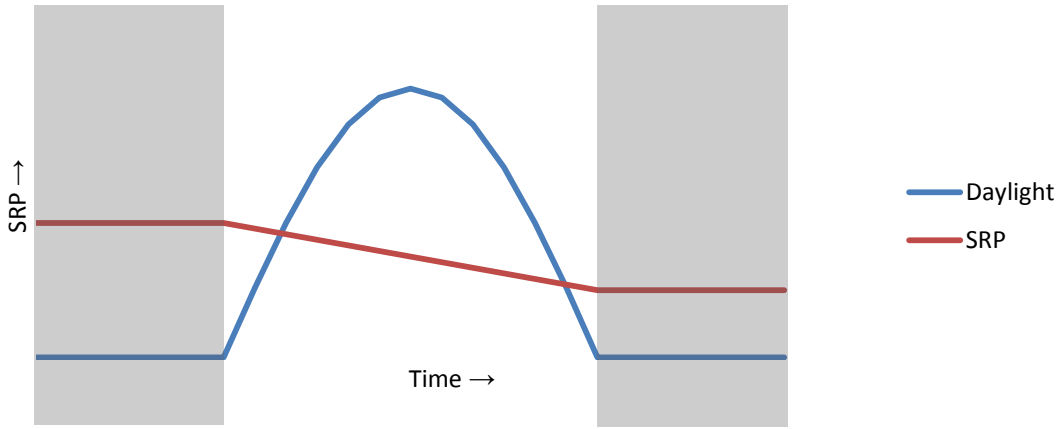

Figure 3.1. Conceptual diagram representing the effects of daylight and higher daytime P demand on SRP concentrations. Through the day, SRP will be assimilated from the water column and decrease the amount of SRP in the water (Bäckström et al. 2002, Mulholland et al. 2005, Forget et al. 2008, Nimick et al. 2011). Dark shaded bars indicate nighttime hours. A recent study has suggested an alternate hypothesis based on the diurnal timing of organismal cell-division with peak SRP assimilation occurring at night simultaneously with ribosomal RNA production (Cohen et al 2013).

The most common inorganic phosphate forms in sediments, sensitive to changes in DO and pH, are those in combination with iron, calcium and magnesium, with some evidence of the importance of manganese-P compounds (Olila et al. 1995, Yao and Millero 1996). Many P compounds are sensitive to changes in oxygen (e.g., iron-bound P; Correll 1998, Shenker et al. 2004, Palmer-Felgate et al. 2011, Erickson et al. 2012) and pH (e.g., apatite, and other calcium-P minerals; Golterman and Meyer 1985). If exposed to depressed DO conditions (< 1.0 mg O_2 L^{-1}), the normally strong binding of hydroxides and oxyhydroxides weakens, and phosphate will diffuse back to the system (Figure 3.2) (Correll 1998, Erickson et al. 2012). It is important to note that 1 mg O_2 L^{-1} is not an absolute value but an estimate based on the sensitivities of many hydroxides and oxyhydroxides, with the potential for some variation in this threshold (Lindsay 1979).

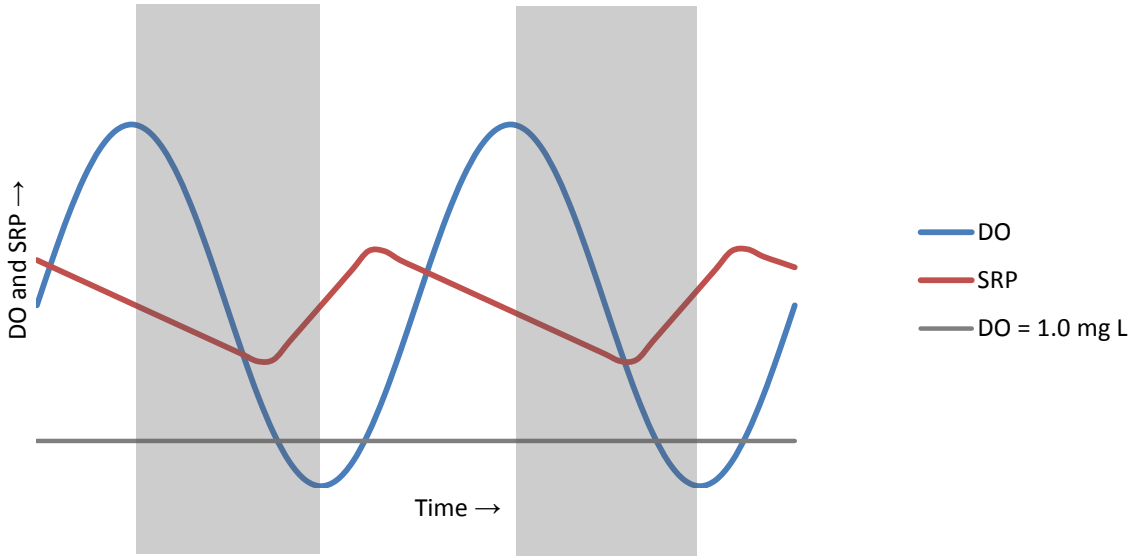

Figure 3.2. Conceptual diagram of the potential effects of diel changes in DO on SRP. When DO concentrations drop below 1.0 mg L^{-1} (Correll 1998, Erickson et al. 2012), redox sensitive P species begin to dissociate and P concentrations in the water column may increase. As waters become more oxygenated during the day, conditions are favorable for redox sensitive P species to adsorb P, decreasing P concentrations during the day (Erickson et al. 2012). Dark shaded bars indicate nighttime hours. Figure assumes instantaneous kinetics.

Generally at high pH (>7.5), calcium and magnesium phosphate compounds decrease in solubility and precipitate (Burns et al. 2001), decreasing P levels in the water column (Figure 3.3). However, some Ca-P species begin to increase in solubility when exposed to a pH >8 (eg. β-tricalcium phosphate; Figure 12.8, Lindsay 1979). At low pH (<6.5), calcium and magnesium phosphate compounds increase in solubility and can release P into the water column

(Goltermann 2001). Diel changes in pH occur in many aquatic ecosystems, with values frequently crossing these ranges in which P chemistry may be affected (e.g., day: 8-9.5 night: 7-8; Reddy 1981).

Given these daily changes in DO and pH, it seems likely that redox and pH-sensitive species, such as phosphate, will also exhibit daily changes. Temperature (affecting microbial uptake and mineralization) may also be important (Golterman 2001).

Recent advances in high frequency *in situ* water quality monitoring instrumentation have made high frequency measurements over diel timescales a more manageable task. On top of many well-characterized diel oscillations (DO, temperature, and pH) (Nimick et al. 2011), high frequency water quality monitoring has begun to shed light on diel changes in nutrient concentrations (Sherson 2012, Cohen et al. 2013). Research on diel changes in P concentrations is relatively rare, and demonstrates varied results, with timing that varies markedly from system to system (Table 3.1). Diel patterns in nitrogen and P concentrations have been observed in large river settings with little work focusing on small stream settings (Scholefield et al. 2005, Pellerin et al. 2009, Volkmar et al. 2011, Baulch et al. 2012, Pellerin et al. 2012, Sherson 2012, Cohen et al. 2013).

Here, we examine diel variability of phosphorus in several small agricultural reservoirs. These reservoirs were constructed as an agricultural beneficial management practice (Reddy et al. 1999, Burford et al. 2011, Tiessen et al. 2011) for enhanced water storage, flood control, and nutrient retention. This type of small lentic water body is also an important land use, covering between 0.1-6% of farmland (Downing et al. 2006). The first purpose of this work was to determine if *in situ* high frequency automated sensors accurately reflect measurements using traditional sampling and analyses methods. The second purpose was to assess whether diel changes in P occurred, and under what conditions.

Table 3.1. Timing of maxima and minima for soluble reactive phosphorus (SRP) in literature.

	SRP maxima	SRP minima	Location	Water body type
Cohen et al. 2013	Afternoon	Midnight	Florida	Large River
Scholfield et al. 2005	2 AM & 2PM	8 AM & 8PM	South West UK	Small River
Sherson 2012	15:00-20:00	5:00-7:00	New Mexico	River
Volkmar et al. 2011	Sunrise	Sunset	California	River

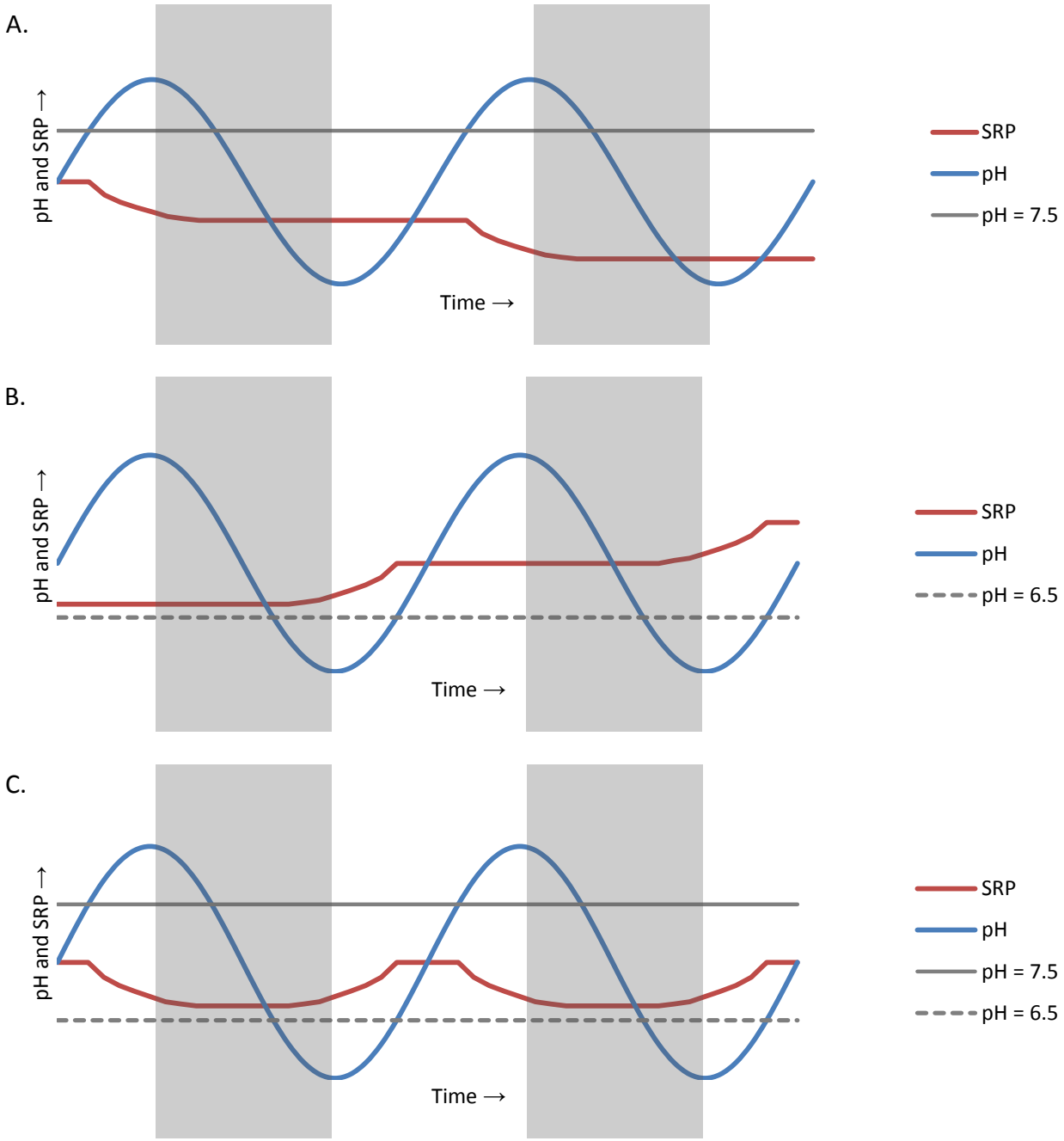

Figure 3.3. Conceptual diagram of potential diel relationships between pH and SRP. A. When pH levels exceed 7.5, indicated by the dark grey solid line, calcium phosphates and magnesium phosphates can precipitate out of solution, decreasing SRP in the water column (Lindsay 1979). B. When pH levels reach below 6.5, indicated by the grey dotted line, calcium and magnesium phosphates become more soluble and can be released back into the water column increasing SRP (Beek and van Riemsdijk 1979; Reddy and DeLaune 2008). C. When both pH thresholds are exceeded on diel timescales, SRP may be released from calcium and magnesium phosphates or precipitated out. Dark shaded bars indicate nighttime hours. All figures assume instantaneous kinetics.

3.2 Materials and Methods

3.2.1 Study Area Characterization

The Tobacco Creek Watershed, in south central Manitoba, Canada, encompasses an area of intense agricultural production, where landowners have constructed headwater dams to help reduce flooding and control downstream nutrient export. Four head water dams were chosen for intense study in the North and South Tobacco Creek Watershed (Figure 3.4). Water depths of the reservoirs were measured at the beginning of the second sampling event (July 2013), approximately 50 days into the 100 day sampling season by transects across the reservoirs. Summer day length in this area can be extremely long, reaching 16.3 hours at its peak in June, with the lowest day length in this study still in excess of 14 hours. Rainfall is typically around 385 mm (Tiessen et al. 2011) between May and October.

3.2.1.1 Reservoir 1 (R1)

Reservoir 1 (49º 23' 45" N 98º 26' 21.7"W) is a multipurpose dam (retains 20% water throughout season) in the North Tobacco Creek Watershed and drains part of a small family operated farm. This reservoir fills during snowmelt and various rain events at the beginning of the season; however, the water levels consistently dropped throughout the growing season. The average reservoir depth was 1.2 m (July 2013 data).

3.2.1.2 Reservoir 2 (R2)

Reservoir 2 (49º 21' 2" N 98º 23' 15" W) is a multipurpose dam in the South Tobacco Creek Watershed, and drains land used for cattle grazing. Like R1, R2 fills during snowmelt and with various rain events but water levels continue to drop even past the inlet. Floating macrophytes (*Lemna sp.*) begin to grow in the mid growing season (early July) and completely cover the reservoir by August. The average depth was 0.95 m (July 2013 data).

3.2.1.3 Reservoir 3 (R3)

The third reservoir (49º 21' 47" N 98º 23' 12" W) is a dry dam (retains ~1 m of water (Tiessen et al. 2011)) and is within a kilometer of R2. R3 however does not have cattle grazing lands. It drains 511 acres, 71% of which is devoted to agriculture. R3 was considerably deeper than the other reservoirs at 2.1 m when measured in July 2013. Floating macrophytes (*Lemna sp.*; Figure A.4 C) begin to grow earlier in the season than R2 and completely cover the reservoir by July.

3.2.1.4 Reservoir 8 (R8)

Reservoir 8 (49º 23’ 4” N 98º 19’ 53” W), the furthest reservoir downstream, is a dry dam, drains a much smaller area of land and is on the lower portion of the Manitoba Escarpment. It is situated close to another reservoir that is just upstream (<500 m). R8 has a considerable riparian zone and is not impacted by floating macrophytes, R8 does not have direct cattle access and it has an average depth of 1.9 m (July 2013). Unlike R1 and R2, the water level at R8 did not decrease but remained relatively constant throughout the field season.

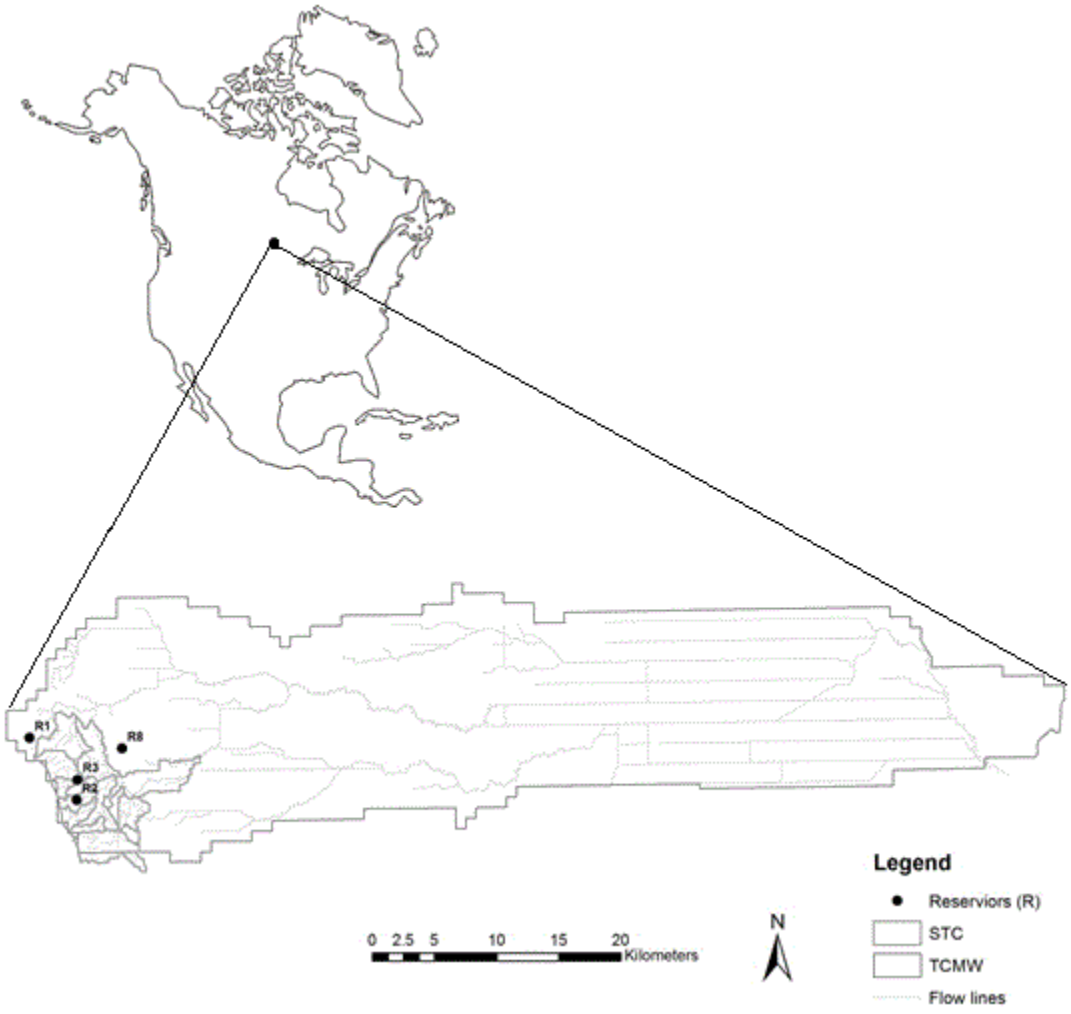

Figure 3.4. Map of the Tobacco Creek Watershed. The South Tobacco Creek Watershed is highlighted in dark gray on the map. Sites where sensors were deployed are marked.

3.2.2 Water Quality Sensor deployment

Three WETLabs Cycle-PO_4 (Cycle-P) (WETLabs, Inc.; Philomath, Oregon, USA) *in situ* dissolved phosphate analyzers were used to determine hourly changes in P concentration in four

separate headwater dams. These instruments measure phosphate concentrations *in situ*, on 10 µM filtered samples via wet chemistry based on EPA Method 365.5. EPA Method 365.5 is an ammonium molybdate, antimony potassium tartrate, and ascorbic method technique for assessing low-level phosphorus concentrations (Zimmermann and Keefe 1997). Water samples are pumped through the intake filter where a 100% transmission value is taken on the sample before they are mixed with reagents. Samples are allowed to react for 17 minutes, after which SRP concentrations are determined at 870 nm with a 5 cm path length (WETLabs 2014). The Cycle-P's specification range is 0.002-0.3 mg P L^{-1}. It can extend to 1.2 mg P L^{-1}; however, values above the specification of 0.3 may be slightly overestimated (WETLabs 2014). Testing based on laboratory standards demonstrates high precision (0.0015 mg P L^{-1}) and accuracy (bias < 0.005 mg P L^{-1}) of the Cycle-P (Cohen et al. 2013).

Cycle-Ps were deployed on a PVC pipe structure that allowed for easy transport while keeping the sample inlet pump ~6 cm above the sediment-water interface (Figure B.1). Care was taken to avoid disturbance of sediment during deployment. All repeated short term and long term deployments throughout the season occurred in the same area of each of the headwater dams with the Cycle-P deployed in water 30-50 cm deep. As necessary, Cycle-Ps were moved deeper into the reservoir to maintain submersion depth in order to keep internal temperatures steady. Where this was done, the Cycle-P was moved deeper in a direction perpendicular to the shoreline, and noted in results.

3.2.3 Chemical analyses and methods validation

To ground-truth automated measurements and supplement the suite of available parameters, manual sampling was performed 2-4 times per day. Water was pumped with a Geotech Geopump™ Peristaltic pump (Geotech Environmental Equipment, Inc., Denver, Colorado, USA) through a tube attached near the Cycle-P intake pump.

3.2.3.1 Soluble Reactive Phosphorus (SRP)

One 35mL water sample was syringe filtered with 25 mm minisart-plus non-sterile 0.45 µm (cellulose acetate) +GF prefilter (Fisher Scientific, Ottawa Ontario) for SRP analysis. Water used for manual SRP analysis was collected in 50 mL glass vials, kept on ice, and analyzed within 36-48 hours, via the molybdate blue method ascorbic acid technique (EPA method 365.1 based on Murphy and Riley 1962 and O'Dell 1993) using a UV-1601PC UV-Visible spectrophotometer (Shimadzu, Laval, QC).

3.2.3.2 SRP filtration methods test

To assess the difference between more standard (0.45 µm) filtration and the Cycle-P filtration (10 µm), additional water samples were gravity filtered through a 10 µm filter in June and July. Samples were analyzed via the same molybdate blue method (Murphy and Riley 1962 and O'Dell 1993) as the 0.45 µm SRP samples. Data were transformed to normality and equal variance and a paired t-test was run to assess differences in filter sizes. The results showed there was no significant difference between the methods (p= 0.713, d.f. =39, paired T-test).

3.2.4 Short-term deployments

Cycle-P and temperature (SBE-37SIP, Seabird, Bellevue, Washington, USA) sensors were deployed during June, July, and August to assess the agreement between hand sampled SRP measurements and measurements taken by the Cycle-P.

3.2.4.1 Comparison between hand and sensor measurements

Cycle-P and temperature sensors were deployed June 1-6, 2013, July 2-7, 2013, and August 2-18, 2013. SRP measurements were taken as close as possible to the Cycle-P hourly measurements 2-4 times a day for 3-5 days (on average, within 20 minutes of Cycle-P sampling) with one intensive pre-dawn sampling event in August. After August 5, 2013 SRP samples were taken once a day (usually in the morning) for the duration of the deployment. Cycle-P and hand measurements, taken in June, July, and until August 12, 2013, were compared using a type II linear regression (Warton et al. 2012; R Project, R Core Team 2013) to determine if the Cycle-P measurements were comparable to measurements of SRP taken by hand. A perfect relationship would be indicated by a slope of one and a y-intercept of zero.

3.2.4.2 Characterization of short-term changes in pH, O_2

Unfortunately, continuous data for pH and DO are not available; however, point-measurements of DO and pH were taken with a Thermo Scientific Orion, Orion 8107 UWMMD Ross Ultra pH/ATC Triode (Thermo Scientific) 2-4 times a day during deployments in June and July. We assessed correlations between SRP and DO and pH using collected hand data throughout the duration of deployment in June and July (Gouhier 2014; R Project, R Core Team 2013).

3.2.5 Long-term deployments: Assessment of diel differences

Cycle-P and temperature sensors were deployed August 1, 2013-August 19, 2013 in R2 and R3 to assess diel differences in SRP in two separate reservoirs. The Cycle-P sampled once

per hour and temperature sensors sampled five times for one minute three times an hour. The five temperature data points per minute were averaged to obtain three values per hour. The Cycle-P deployed at R3 was moved deeper into the reservoir (August 12, 2013 8:00) to maintain necessary submersion. This provided a natural divide in the data. The first half of the deployment characterized by shallower water (< 1 m) occurred from August 2-12, 2013, and is referred to as R3-1, while the second half of the deployment, characterized by deeper water (≥ 1 m) occurred from August 12-18, 2013 and is referred to as R3-2. Point measurements for DO and pH were with the same sampling design as stated in section 3.2.4.1; however, samples were taken in the same area of R3 regardless of where the Cycle-P was deployed to minimize sediment disturbance.

To determine if diel patterns could be identified in Cycle-P data, wavelet analysis (R Project, R Core Team 2013) was used to assess both amplitude and periodicity of SRP and water temperature. Wavelet analysis is ideal for time series ecological data sets that exhibit non-stationarity because unlike traditional correlation techniques that assume statistical stationarity, wavelet analysis is not limited by this assumption (Cazelles et al. 2008). Systems with transient components, such as those in this study, are impacted by many factors, such as weather or cattle influences, that can lead to signals varying in amplitude and frequency over longer periods of time.

Due to the length of the short term deployments there is not enough data to support wavelet analysis. However, time series were adequate for wavelet analyses in longer-term deployments. Longer-term data were linearly interpolated to equal sampling frequencies (Appendix B; Figures B.6-8) in advance of these analyses. Wavelet power spectra were generated for temperature and SRP for R2, and for R3-1 and R3-2. The significance of the power spectra was determined through chi square tests. These spectra were then combined to form a wavelet coherence figure to determine whether there was significant coherence between temperature and SRP based on 500 Monte Carlo simulations and significant phase relationships.

3.2.6 Percent variation equations

Percent variation equations were used to determine the average diel percent variation, equation 3.1 and the mean deviation, equation 3.2, for the Cycle-P data.

Percent variation between maxima and minima was calculated as follows:

$$\frac{(Average\ daily\ maximum\ SRP - Average\ daily\ minimum\ SRP)}{Overall\ average\ SRP} \times 100 = \% \qquad (3.1)$$

Mean deviation calculated as follows:

$$mean\ deviation = \frac{\sum |x - mean|}{total\ number\ of\ data\ points} \quad (3.2)$$

3.3 Results

3.3.1 Sensor validation

Comparison between Cycle-P data and manual sampling of SRP shows a generally good fit. Relationships between Cycle-P and manual SRP measurements at sites R1 and R3 showed the 95% confidence interval (CI) for the y-intercept overlapped zero (Table 3.2). However, R2 showed an offset with an intercept of 0.118 ± 0.64. Two-thirds of the measures in R2 were measured above the 0.3 mg L^{-1} specification range on the cycle while just over half of the values were above 0.3 mg L^{-1} when taken by hand. In all cases, the confidence interval for the slope of the relationship between Cycle-P data and manual-sampling data overlapped one.

Table 3.2 Type II regression slope, intercept (95% Confidence Interval; CI), and r^2 values of Cycle-P soluble reactive phosphorus (SRP) data on hand sampled SRP data, and concentration range of hand sampled SRP mg L^{-1} data. Data for available sensor and hand soluble reactive phosphorus data taken in June, July, and August.

Site	Slope (CI)	Intercept (CI)	n	r^2	SRP Concentration Range (mg L^{-1})
R1	1.017 (0.891 – 1.161)	-0.004 (-0.017 - 0.010)	13	0.962	0.054 - 0.160
R2	0.830 (0.637 - 1.069)	0.118 (0.054 - 0.182)	36	0.654	0.253 - 0.472
R3	1.133 (0.771 - 1.698)	0.026 (-0.008 - 0.061)	14	0.737	0.067 - 0.138

3.3.2 Short term deployments: relationship between SRP, pH and DO data

No clear diel trends in SRP were observed across reservoirs R1 and R2 in June (Figures 3.5-3.6). One reservoir showed a general decrease in SRP throughout the sampling period (R1; Figure 3.5), while R2 showed steady values (0.017 mean deviation) throughout the duration of deployment (Figure 3.6). In R1 three unexplained SRP values near zero (Figure 3.5) were recorded during the first three days of deployment (June 2 at 21:00, June 3 at 1:00, and June 4 at 1:00).

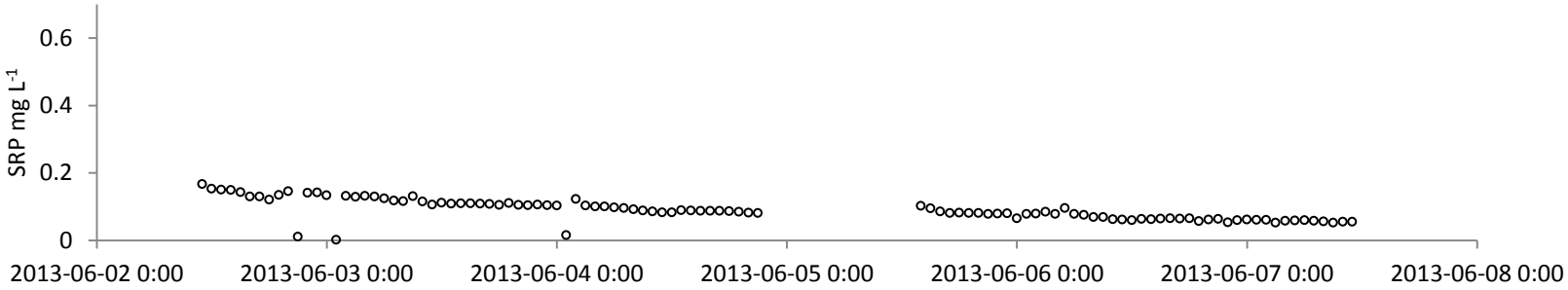

Figure 3.5 R1 soluble reactive phosphorus concentration from Cycle-P in June 2013.

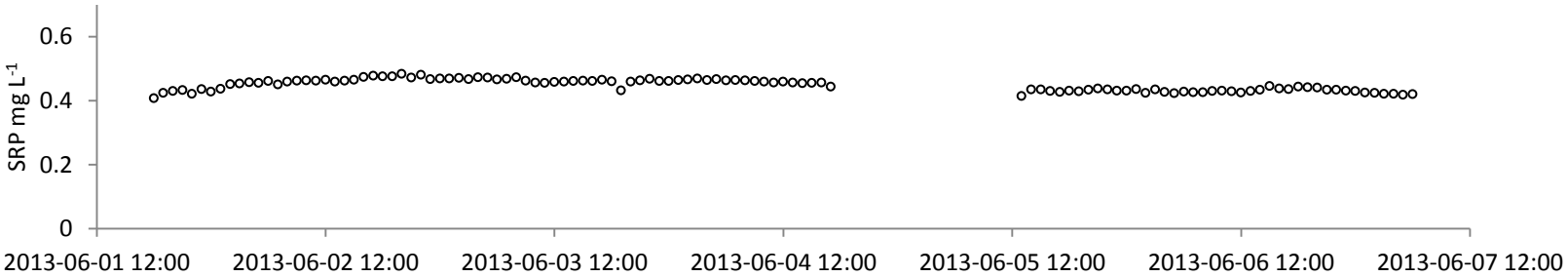

Figure 3.6 R2 soluble reactive phosphorus concentrations from Cycle-P in June 2013.

Point measurements of DO values ranged from 7.1-10.4 mg L^{-1} in the three reservoirs in June (Table 3.3). pH values were in excess of 7.5 three times in R1 and two times in R2 and below 6.5 once in both R1 and R2 (Tables B.2 and B.3). SRP was significantly negatively correlated to DO in R1 (Pearson's Product Moment Correlation, r=-0.588, p=0.035) while SRP was significantly positively correlated to pH in R8 (Pearson's Product Moment Correlation, r=0.852, p<0.001). No correlations between DO or pH and SRP were observed in R2 in June (Table 3.3)

In July, DO values in R1 were notably lower than in June with point DO measurements showing values falling below 1 mg L^{-1}. Dissolved oxygen values in R2 were more dynamic in July than June (Table 3.3; Appendix B, Tables B.5-7, Figure B.3). Dissolved oxygen levels in R8 were comparable to those values observed in June. pH levels in all three reservoirs ranged from 7.14-8.05 with approximately one-third of point measurements below 7.5. SRP was significantly negatively related to DO in R1 (Pearson's Product Moment Correlation, r=-0.670, p=0.049) and significantly negatively correlated to pH in R2 (Pearson's Product Moment Correlation, r=-0.733, p=0.025). Due to sensor failure, high frequency SRP data was only recorded in R2. Two large scale disturbances were recorded in R2 towards the beginning and the end of the data set (Figure 3.7). R2 data showed possible bimodal daily SRP peaks, the first occurring between 8:00-10:00 and the second occurring between 18:00-20:00, that exhibited a 0.087 mean deviation, approximately five times higher than the previous month.

In August, only R2 and R3 were sampled due to failure of the cycle deployed in R1. Point measurements of DO in August showed levels below 1 mg L^{-1} in only R3, values in R2 were measured at 1.7 mg L^{-1} (additional data found in Appendix B, Tables B.8-9, Figure B.4). In R2 two point measurements of pH in total were in excess of 7.5, both occurring on the same day in the mid-afternoon and early evening (14:00 and 20:00). Conversely in R3, one third of pH values were above 7.5, with these values occurring in the early afternoon throughout the duration of the deployment. In August, SRP was significantly negatively correlated to DO in R3-1 (Pearson's Product Moment Correlation, r=-0.546, p=0.043). No significant relationships between SRP and DO or pH were observed in the R3-2 or R2 deployments (Table 3.3).

Table 3.3 Summary table of short and long term deployments for dissolved oxygen (DO), pH, temperature (ºC), hand measured soluble reactive phosphorus (SRP) mg L^{-1}, Cycle-P SRP mg L^{-1}, Pearson's Product moment correlations between hand measured SRP and DO, and hand measured SRP and pH, and discernable SRP pattern. N/A indicates sensor failure, with no data collected.

Deployment Date	Reservoir	DO Range	pH Range	Temp Range	SRP range (hand)	SRP range (Cycle-P)	SRP and DO correlation	SRP and pH correlation	SRP Pattern
June 1-7	R1	7.5-10.4	6.45-7.91	9.9-17.0	0.060-0.271	0.007-0.167	-0.588*	0.291	No diel signal
June 1-7	R2	8.6-10.4	6.52-7.75	11.1-23.3	0.354-0.428	0.407-0.483	-0.528	-0.124	No diel signal
June 1-7	R8	6.5-9.5	6.46-7.53	11.1-21.2	0.058-0.152	N/A	0.265	0.852***	N/A
July 2-5	R1	0.4-4.4	7.14-7.69	20.0-26.0	0.335-0.486	N/A	-0.670*	-0.644	N/A
July 2-5	R2	2.5-12.8	7.37-8.15	22.6-26.9	0.222-0.301	0.210-0.848	-0.433	-0.733*	Bimodal
July 3-6	R8	7.7-8.9	7.48-7.96	21.8-28.1	0.001-0.022	N/A	0.291	0.263	N/A
August 2-18	R2	0.5-6.4	7.28-7.77	14.4-21.5	0.178-0.305	0.202-0.550	0.415	0.344	Diel signal
August 2-12	R3-1	0.9-2.5	7.35-7.60	13.9-19.8	0.010-0.235	0.068-0.173	-0.546*	-0.487	Diel signal
August 12-18	R3-2	0.2-1.4	N/A	12.9-18.7	0.035-0.125	0.235-0.776	-0.560	N/A	Diel signal

*Significant at the 0.05 probability level
**Significant at the 0.01 probability level
***Significant at the 0.001 probability level

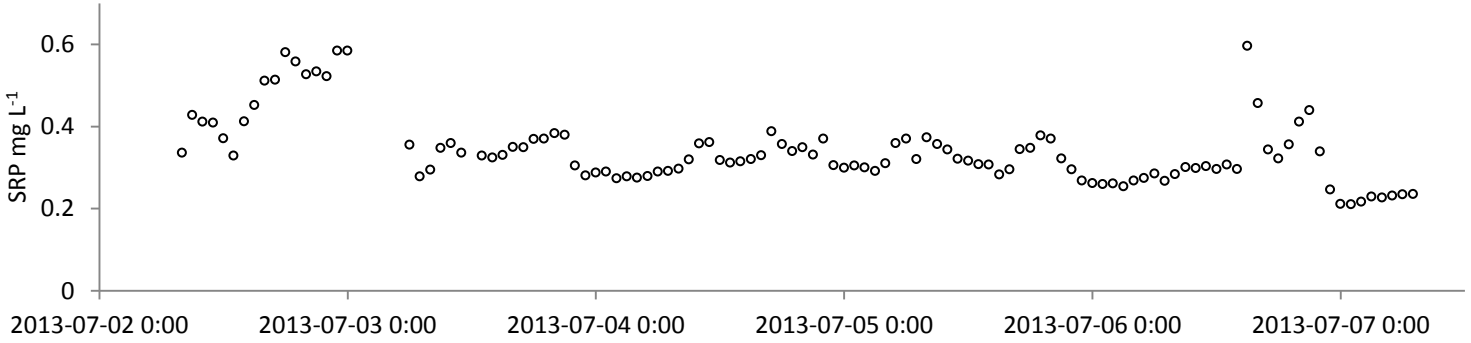

Figure 3.7 R2 soluble reactive phosphorus concentrations from Cycle-P in July 2013.

3.3.3 Long term deployments: Wavelet approaches to assess diel differences

In August reservoirs R2 and R3 both showed significant temporal patterns (warm colors within the solid black contour line) in Cycle-P SRP (Chi-Square test; Figures 3.8 D, 3.9 D, 3.10 D) and temperature (Figures 3.8 C, 3.9 C, 3.10 C) with a periodicity approximately equal to one day, although a two day period was also found to be significant (Figures 3.8 D, 3.9 C, 3.9 D). Coherence, the direct measure of the correlation, between the non-stationary temperature and SRP signals was either significant and slightly out of phase (temperature leading P by ~6 hours) or lacked a significant phase relationship in all three reservoirs. During a major rain event (August 4-6, 2013) the relationship between temperature and SRP appeared to down and was no longer significant in R2 and R3-1 (shown by arrows in Figures 3.8 E, 3.9 E). In R3-2 (unaffected by the rainfall), temperature significantly led phosphorus (~6 hours) throughout the duration of the deployment (shown by arrows Figure 3.10 E).

The timing of peak phosphorus concentrations, recorded by the Cycle-P varied between the two reservoirs used for longer-term deployments. R2 had a singular diel trend (with the exception of the rainfall-affected period) that lasted throughout the duration of deployment. Low values were typically clustered around mid-morning hours 5:00-8:00 with some troughs lasting until 12:00. Peak values occurred at night between 21:00-2:00 with one peak occurring around 10:00. Over the deployment, the % variation between average maximum and minimum values was 64% (equation 3.1). The Cycle-P that was deployed in R3 had to be moved to deeper water halfway through the field deployment. Associated with that move, R3 showed two distinct diel trends for SRP, before (R3-1) and after (R3-2) the instrument was moved (August 12, 2013 8:00). R3-1 had higher variability in timing of maximum and minimum values, with maxima typically ranging between late evening and early morning (22:00-2:00) with occasional peaks occurring around mid-day. Minima ranged from early to late morning (5:00-7:00) with one peak at 17:00-20:00. The percent variation between average maximum and minimum values of SRP values was 41%. R3-2 showed more consistent timing of values after August 14, 2013 with maxima occurring in the early morning hours (3:00-5:00) and minima occurring in the late afternoon or early evening (15:00-19:00). Average percent variation between maximum and minimum SRP values was 47%.

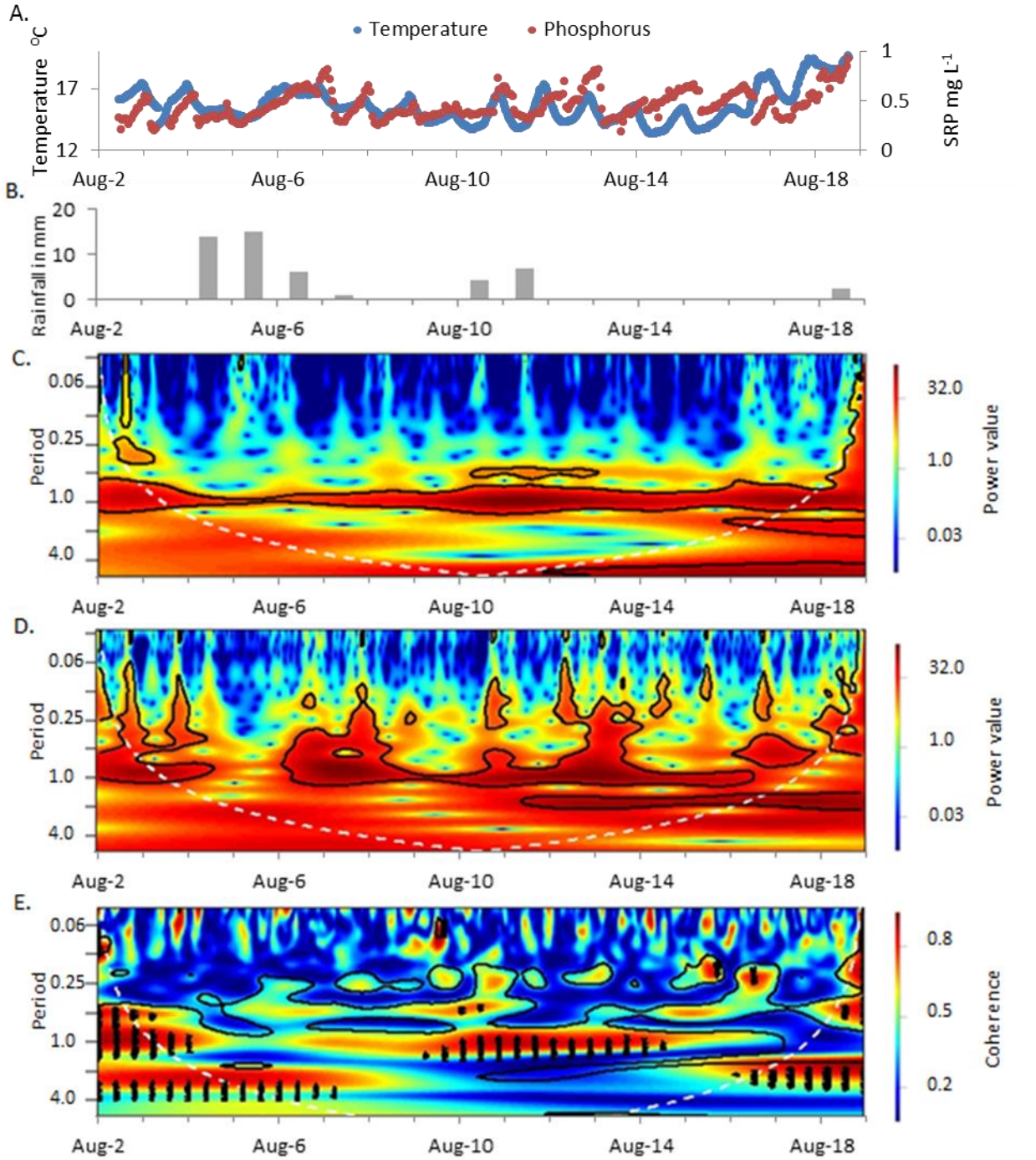

Figure 3.8 Temperature, rainfall, and the association between soluble reactive phosphorus (SRP) and temperature in reservoir R2. Tick marks indicate midnight for each day of deployment. A. Time series data for temperature and SRP. B. Average rainfall over time in mm. C. Wavelet power analysis for temperature. D. Wavelet power analysis for SRP. In both C and D colors code from dark blue (low values) to dark red (high values) and the white dashed line indicates the cone of influence that separates the area not influenced by edge effects. The solid dark lines show the α=0.05 significance levels computed based on Chi-square distributions. P-values within contours made by the dark line are less than 0.05. E. Coherence between temperature and SRP time series. Period indicates days. Colors code from dark blue (low values) to dark red (high values) and the white dashed line indicates the cone of influence that separates the area not influenced by edge effects. The solid dark lines show the α=0.05 significance levels computed based on 500 Monte Carlo simulations. P-values within the area made by the dark line are less than 0.05. Arrows indicate significant coherence.

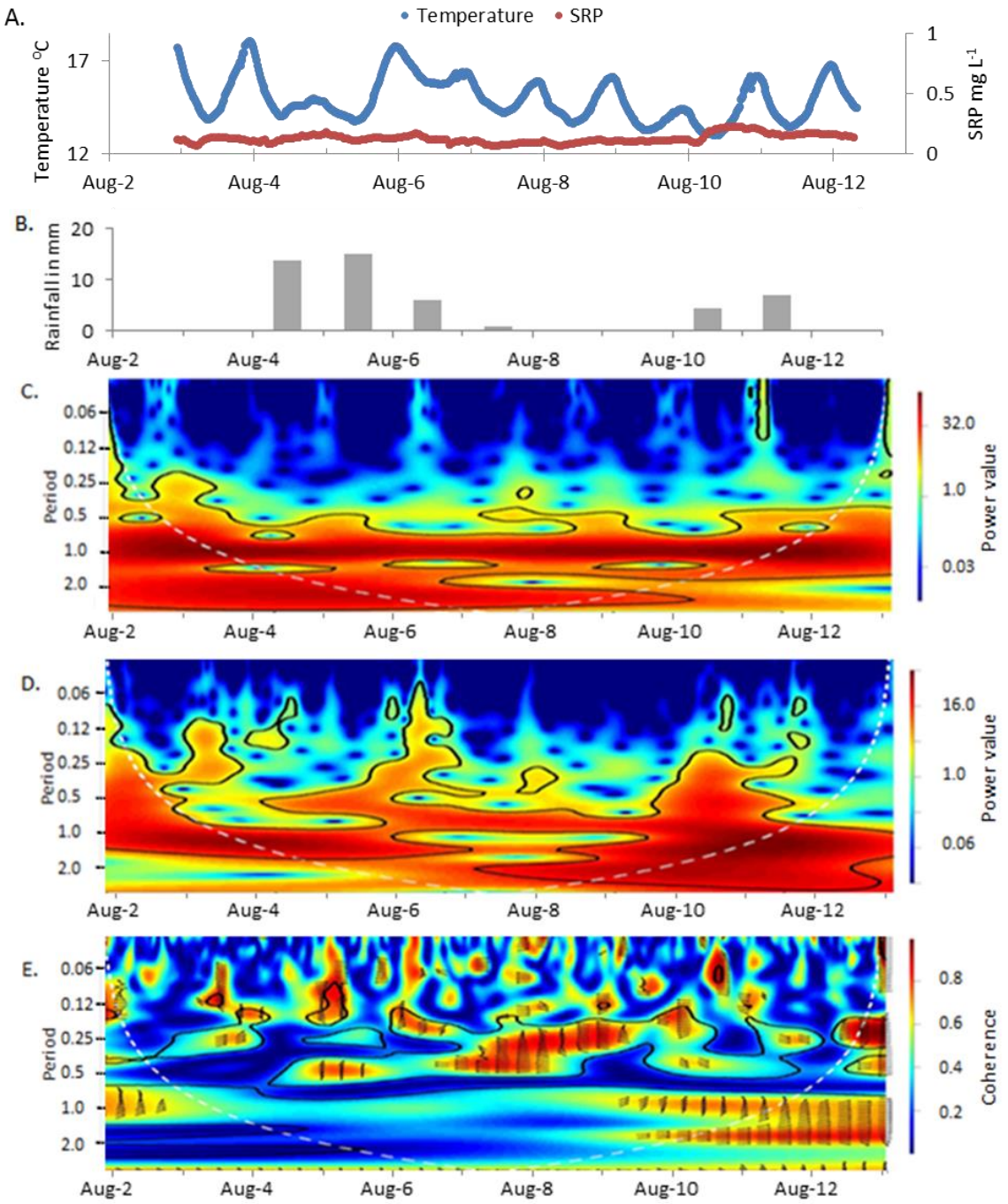

Figure 3.9 Temperature, rainfall, and the association between soluble reactive phosphorus (SRP) and temperature in reservoir R3-1. Tick marks indicate midnight for each day of deployment. A. Time series data for temperature and SRP. B. Average rainfall over time in mm. C. Wavelet power analysis for temperature. D. Wavelet power analysis for SRP. In both C and D colors code from dark blue (low values) to dark red (high values) and the white dashed line indicates the cone of influence that separates the area not influenced by edge effects. The solid dark lines show the α=0.05 significance levels computed based on Chi-square distributions. P-values within contours made by the dark line are less than 0.05. E. Coherence between temperature and SRP time series. Period indicates days. Colors code from dark blue (low values) to dark red (high values) and the white dashed line indicates the cone of influence that separates the area not influenced by edge effects. The solid dark lines show the α=0.05 significance levels computed based on 500 Monte Carlo simulations. P-values within the area made by the dark line are less than 0.05. Arrows indicate significant coherence.

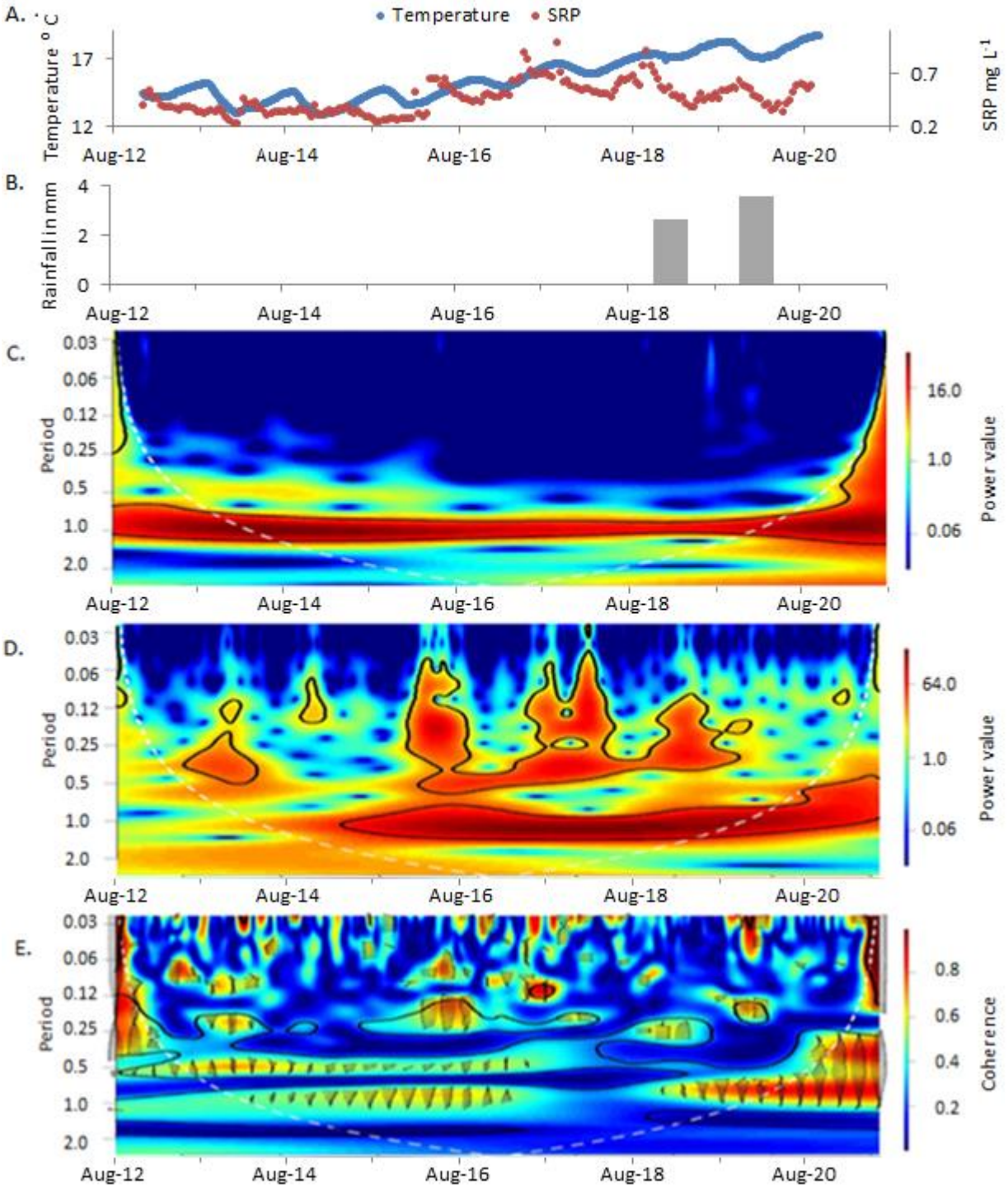

Figure 3.10 Temperature, rainfall, and the association between soluble reactive phosphorus (SRP) and temperature in reservoir R3-2. Tick marks indicate midnight for each day of deployment. A. Time series data for temperature and SRP. B. Average rainfall over time in mm. C. Wavelet power analysis for temperature. D. Wavelet power analysis for SRP. In both C and D colors code from dark blue (low values) to dark red (high values) and the white dashed line indicates the cone of influence that separates the area not influenced by edge effects. The solid dark lines show the α=0.05 significance levels computed based on Chi-square distributions. P-values within contours made by the dark line are less than 0.05. E. Coherence between temperature and SRP time series. Period indicates days. Colors code from dark blue (low values) to dark red (high values) and the white dashed line indicates the cone of influence that separates the area not influenced by edge effects. The solid dark lines show the α=0.05 significance levels computed based on 500 Monte Carlo simulations. P-values within the area made by the dark line are less than 0.05. Arrows indicate significant coherence.

3.4 Discussion

3.4.1 Sensor Validation:

The Cycle-Ps used in this study showed reasonable agreement to traditional, manual sampling and analyses techniques (slope near one, intercept generally near zero) with correlation coefficients ranging from 0.654-0.962. There was no evidence that the difference in filter size between the methods affected the results; however repeated methods tests later in the summer would be beneficial. Within R2, the elevated intercept may be related to concentrations that exceeded the normal operating range of the Cycle-P.

It is possible that differences in analytical methods may also have contributed to differences between hand and Cycle-P SRP concentrations, and affected correlations. Both hand and Cycle-P methods are based on the Murphy and Riley (1962) method, however, each method uses different concentrations of reactants. The Cycle-P method is more acidic using 2.55 M H_2SO_4 while the method used for hand samples was less acidic using 1.57 M H_2SO_4. Due to the heterogeneous nature of SRP, acidity has the potential to affect measured concentrations (Esterby and Bertam, 1993). A stronger acid has the potential to liberate more molybdate-reactive P (Jarvie et al 1999); although a systematic difference was not apparent here. Matrix chemistry is thought by some to be more important than acidity and reagent concentrations (Tarapchak et al. 1982); however, due to the sampling regime, differences in water matrix chemistries in our study are presumed to be negligible. Although we observed variable r^2 values it is not clear why R1 had the best fit, however it is important to note this reservoir exhibited intermediate water chemistry throughout deployment (Table A.1).

3.4.2 Short term deployments: Characterization between pH and DO data

During the June deployment, which followed a major rain event (115 mm May 28-31 2013, farmer network monitoring data, Don Cruikshank, personal communication, 24 September, 2014), SRP showed a steady decrease throughout the sampling period in R1 and R8, which may be due to suspended particles and sediment settling after the water pulse generated by the previous rain event. However, R2 displayed little increase or decrease (0.017 mean deviation). There was no evidence of diel variation in SRP in any of the reservoirs. Temperatures remained low, while DO values were the highest of the field season. Although the inverse relationship observed in R1 between DO and SRP is consistent with what we would expect to see in a system with redox sensitive P species, it is likely redox conditions did not

occur, and autotrophic uptake may be the more likely driver of this relationship. pH levels had the greatest variability in June, sufficient for both Ca-bound P and Mg bound P release (low pH 6.5) and uptake (high pH 7.5) (Table 3.3; Golterman 2001). A positive correlation between SRP and pH was seen in R8, which is inconsistent with patterns driven by precipitation of calcium or magnesium phosphates at high pH. Results for this month suggest that hydrologic flushing from the flood pulse was the dominant control on SRP concentrations.

During the July short term deployment, continuous data were only available from R2, due to cycle P failure in R1 and R8. In R2 it appeared that twice daily peaks were occurring in the morning (8:00-10:00) and in the evening (18:00-20:00). Although these patterns in R2 could reflect periodic cattle disturbance (cattle had direct access to the site), this type of "saw tooth", twice daily, maxima and minima values has been observed in other systems (Scholefield et al. 2005). Point measures of DO in R1 and R2 suggest it is possible that the threshold of redox control over SRP was reached. In R1 this is consistent with the significant inverse relationship observed between DO and SRP; however, the lack of high frequency data makes it unclear whether diel variation in SRP was occurring. Point pH measures in all three reservoirs R1, R2, and R8 suggest that levels needed for pH-sensitive P species (Ca-bound and Mg-bound P) to precipitate were reached. This mechanism is consistent with the inverse relationship seen in R2 between pH and SRP, although the relationship was not observed in R1 or R8.

3.4.3 Long-term deployments: Assessment of diel differences

August was the only month where consistent diel patterns in SRP were recorded (one day periodicity). During all three deployments there were short periods of statistically significant, unexplained periodicity at much higher frequencies.

3.4.3.1 Biological influences

Increased P uptake has been linked to increased primary productivity in aquatic systems with uptake rates reported to be higher during cloud-free and mid-day hours (Mulholland et al. 2006). Uptake of nutrients is typically thought to be dominant for primary producers during the day, and this would result in a slow decrease in P concentrations throughout the day and stabilization at night (Figure 3.1), consistent with patterns seen in R3-2 in August (and aforementioned correlations between SRP and DO in R1 in June). Previous work in the San Joaquin River reported a pattern consistent with daytime biologic uptake of nutrients, with minimum values at sunset and maximum values at sunrise (Volkmar et al. 2011). However, the

timing of SRP maxima and minima values in R2 and R3-1, inconsistent with algal assimilation in both the daytime and nighttime, suggests that biological assimilation may not be the primary factor influencing SRP concentrations in these systems. However, it may be that the timing of autotrophic uptake as a driver for diel variation in nutrients may not be straightforward. For example, recent work has also hypothesized an important nighttime demand for nutrients potentially controlled by the diel timing of organismal cell-division (Cohen et al. 2013).

3.4.3.2 Chemical Influences

Diel variation in primary productivity, with daytime maxima, and nighttime minima (Odum 1956) may affect SRP concentrations. Point measurements of DO (< 1.0 mg L^{-1}) suggest that it is likely that thresholds for redox control over SRP were reached in R2 and during both deployments at R3. Based on this, and assuming instantaneous kinetics, we would expect to see metal oxide-bound P species liberated around dawn as DO values reach minima levels past the threshold for redox control (Grobbelaar and House 1995, Golterman 2001; Figure 3.2). Measured SRP values in R3-2 were consistent with timing of potential metal oxide bound P release (Golterman 2001). However, measured SRP maxima and minima values were not consistent with this timing in R2 and R3-1.

Similar to DO values, we expected pH values to follow a similar pattern of high values at dusk and low values at dawn as a result of diel changes in CO_2 (Odum 1956). pH point measurements in R3 suggest that levels needed for precipitation of pH sensitive P species (mostly Calcium bound P and Magnesium bound P) were likely reached (pH 7.5; Golterman 2004), potentially removing P from the water column (Figure 3.3A), consistent with patterns of SRP minima at the time of anticipated pH maxima in R3-2. The timing of SRP maxima and minima in R2 and R3-1 however suggest that pH may be secondary to other factors influencing SRP.

3.4.3.3 Physical Influences

Physical influences on the hydrology of the area may also influence potential SRP cycling. Breakdowns in the one day period of oscillations in P concentrations appeared to result from a major rainfall event, although a smaller rainfall event did not correspond to a breakdown in the daily P pattern. During the larger rain event, flow-through dynamics may have overwhelmed processes affecting diel changes in SRP. Additionally, longer rain events with overcast skies would also influence SRP cycling by decreasing the amount of algal assimilation

occurring (Mulholland et al. 2005) and minimizing primary productivity, leading to more muted diel cycles in DO and pH. Though not studied here, groundwater inputs may contribute to fluctuations seen in SRP values (Lundquist and Cayan 2002).

3.4.3.4 Timing of diel changes

The timing of SRP maxima and minima during long term deployment in R3-2 is consistent with what we would expect from a system with dominated control by algal assimilation, or by DO (metal oxide bound) and pH sensitive (Ca and Mg bound) P species. However, timing in R2 and R3-1 is inconsistent with control of the same factors. Timing of minima for SRP for R2 and R3-1 was similar to those observed in the East Fork Jemez River, New Mexico, USA (Sherson 2012) with minima values occurring between 6:00 and 8:00 while our values occurred between 5:00-8:00. A different study in the River Taw observed two maxima and minima peaks per day with one max value occurring at 2:00 around the time those maxima values in R2 and R3-1 were occurring. Due to the varied timing of SRP minima and maxima between reservoirs, it is clear no single factor drives the changes observed in P concentrations in our study. There is likely a combination of physical, chemical, and biological factors influencing the reservoirs.

3.5 Conclusions

Water quality monitoring sensors represent an important tool to gain new insights into the timescale upon which water quality changes. Data from the Cycle-P displayed a relatively consistent fit with water samples collected and analyzed by hand. However, point measurements should be taken to ground-truth Cycle-P measurements over time. Caution should be used in interpreting Cycle-P data as absolute concentration values exceeded the specification limit of 0.3 mg L^{-1}, which affects the reliability of the instrument in very high nutrient waters such as these.

In our study diel changes were seen in one reservoir in July and two separate reservoirs in August, but were not observed earlier in the summer. Although August DO concentrations reached levels at which release could occur, only R3-2 showed timing of SRP maxima and minima consistent with the release and uptake of redox sensitive P species. Within the remaining two deployments (R2 and R3-1) patterns and timing of changes in SRP, pH and DO were not consistent with any simple, single driver, but instead suggest multiple factors affecting SRP, with the potential for time lags blurring these responses. This is consistent with past research, where major differences in timing of SRP maxima and minima, and differences in apparent drivers, have been reported (Scholefield et al. 2005, Sherson 2012, Cohen et al. 2013). We note that we do not know the extent of spatial variation in dissolved P across R3, and importantly, whether any depth or spatial related variations occur. Given different results in R3-1 and R3-2, we suggest concurrent deployments of sensors within the same small system may yield further insights into temporal and spatial scales of P cycling, and better constrain whether, where, and when diel changes in SRP may occur.

Variation in water chemistry in our study occurred on hourly, daily, and monthly timescales. We found that diel changes in SRP were occurring, and that these could bias results from monitoring programs reliant on typical sampling frequencies (once daily, weekly, or monthly). These results suggest that future studies which rely upon singular grab samples for P sampling should aim to sample in the mid-morning (9:00-11:00), a time with limited influence by both maxima or minima values in this study (average 4.5% underestimation of mean values) and other cited studies in this thesis. However, it is worth noting that although a bias may result with early morning or afternoon sampling (e.g., sampling at 6 am in this study would lead to an average 16.1% underestimation of mean SRP concentrations) the magnitude of this bias is much less than reported for nitrogen species (Baulch et al. 2011).

In order to tease apart the complex interactions of the direct biotic effects on SRP (primary productivity-uptake), effects of biotic activity (changes in DO and pH), and influences of physical variables (rainfall events, ground water inputs) on the system, additional water quality measurements would be beneficial. High frequency nutrient monitoring should be implemented in conjunction with hourly, or sub hourly samples of DO, pH, metal ions (Ca, Fe, Mg), chlorophyll, temperature, sunlight, and rain. In addition, given the sensitivity of these, and other systems, to rain events, ideal sampling designs to understand diel variation would focus on periods of low or no rainfall.

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CHAPTER 4: General Conclusions

Reservoirs and downstream stream pools (depositional areas) in the Tobacco Creek Watershed can mediate phosphorus (P) removal from overlying waters via sorption to sediments. The majority of the 15 sites in this study (eight headwater dams and seven stream pools) exhibited similar behavior and acted as a sink of P with the potential to take up more P as the season continued. This is consistent with previous findings in the area of significant nutrient retention capacity of headwater dams (Tiessen et al. 2011). Similarities in temporal EPC_0 dynamics are consistent with previous studies (Belmont et al. 2009, McDaniel et al. 2009). Relatively constant P sorption in space and time can be linked to similarities in sediment composition (high clay content) as well as similarities in water quality parameters such as dissolved cations, dissolved oxygen, conductivity, and dissolved organic carbon.

Importantly, there may be opportunities to maximize phosphorus retention by sediments via increases in residence time which would increase the time for sediment-water interactions that maximize P uptake (Froelich 1988). In addition, areas in streams or reservoirs with increased residence time tend to accumulate fine sediments, which tend to have high rates of P uptake, maximizing P sorption from the water column (Haggard et al. 1999, McDaniel et al. 2009). Stream pools in the lower watershed exhibit many of the same qualities of reservoirs associated with high P retention. As such, these pools may present an opportunity for further development of BMPs, for example, by increasing the submerged surface area and hence area of sediment available for P sorption.

Despite knowledge that these reservoirs can act as P sinks, little was known regarding temporal variation in phosphorus concentrations in these reservoirs, which contribute to error in estimates of mean conditions, and mass balances. The reservoirs in our study did show daily fluctuation in water column P throughout the sampling period but a diel signal was only observed during the month of August. One Cycle-P deployment exhibited P fluctuations consistent in timing with changes in primary production (dissolved oxygen and pH) thought by some to be the driving factors behind changes in diel P concentrations (Volkmar et al. 2011). Two Cycle-P deployments showed daily fluctuations inconsistent with the timing of changes in primary production, which have also been demonstrated in past work in rivers (Sherson 2012, Cohen et al. 2013). This suggests other mechanisms of P retention and release are also at play.

Phosphorus sorption was related to sediment size, DOC, OMS, and Ca^{2+}, while short-term daily fluctuations were related to daily fluctuations in DO, pH and, algal uptake. Both parts of my project give insight into P cycling and allow for a more comprehensive view of P dynamics by examining both monthly (sediment) and daily (water column) changes, providing an in depth look into select mechanisms impacting P sorption and retention through space and time.

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APPENDIX A

A.1 Soluble reactive phosphorus duplicate analysis

To determine the effects of freezing filtered water samples on SRP analysis, duplicate soluble reactive phosphorus samples were collected at each site during May 2013. Thirty-five mL water samples were syringe filtered with 25 mm minisart-plus non-sterile 0.45 µm (cellulose acetate) +GF prefilter. One sample was kept on ice while the second was frozen. Both samples were analyzed within 36-48 hours, via the molybdate blue method (Murphy and Riley 1962) using a UV-1601PC UV-Visible spectrophotometer. A paired t-test indicated no significant difference between frozen and unfrozen samples ($p=0.828$, d.f. =9).

A.2 Sediment freezing test

Sediment was gathered at each study site throughout the field season. EPC_0 experiments were run on freshly collected samples (<5 days). A subset of sediment was frozen at -40ºC to determine if freezing had an effect on EPC_0 values. EPC_0 experiments were completed on one site (P1, August 2013) stored at -40ºC for six months. A paired t-test was used to compare frozen EPC_0 data to freshly collected EPC_0 data. Percent variation was also calculated to compare results. EPC_0, partition coefficient, distribution coefficient, and reactive soil pools, for the original equilibrium isotherm (unfrozen) were 0.046 mg L^{-1}, 0.962, 0.229 $m^3 kg^{-1}$, and 10.40 mg kg^{-1}, respectively and the frozen isotherm was 0.047 mg L^{-1}, 0.960, 0.223 $m^3 kg^{-1}$, and 10.42 mg kg^{-1}, respectively (Figure A.1). The coefficient of variation (CV) between the two treatments for EPC_0, partition coefficient, distribution coefficient, and reactive soil pools were, 3.4 %, 0.3 %, 2.5 % and 0.2 %. A paired t-test comparing sorption values for each initial P concentration (0, 0.05 0.1, 0.5, and 1 mg L^{-1}), showed no significant difference between EPC_0 values from the two methods ($p= 0.32$ d.f. =4). Triplicate unfrozen samples showed an EPC_0 CV of 7.4 %

A.3 Variability among replicate EPC_0 incubations:

Single samples were typically run for EPC_0, due to the time consuming nature of this analysis (Jarvie et al. 2005). Four replicate EPC_0 experiments were run for site P1 (sampling date August 5, 2013) to assess variability in EPC_0 determinations. Variation in P sorption increases as initial P concentrations increase (Figure A.2). EPC_0 values for replicates were 0.046, 0.050, and 0.053 mg P L^{-1}. The resulting CV was 7.4%. The standard error of the slope was 0.58. Partition coefficients were 0.962, 0.958, and 0.954, respectively with a CV of 0.45%.

Distribution coefficients were 0.229, 0.211, and 0.183 $m^3 kg^{-1}$ respectively with a CV of 11.2% and the reactive soil pools were 10.40, 7.74, and 9.80 mg kg^{-1} respectively with a CV of 15.0%.

A.4 Supporting information

A schematic of sediment collection can be found in Figure A.3 while photos of each site can be found in Figure A.4. Summary data for soluble reactive phosphorus (SRP), total phosphorus (TP), alkalinity, calcium ions (Ca^{2+}), magnesium ions (Mg^{2+}), pH, dissolved oxygen (DO), % organic matter in sediment (OMS), dissolved organic carbon (DOC), conductivity (cond) and % fines in total sediment are presented in the main text; however, comprehensive data for the previously mentioned water quality parameters for each month is also reported here (Table A.1).

A.5 Metals bound to sediment quality control procedures

PACS-2 was used as a standard reference material to assess precision and recovery of the aqua regia digestion for metal determination by MP-AES. PACS-2 is a certified reference material (CRM), with data available for total digestion (Microwave acid digested with HF, HNO_3, and $HClO_4$) but partial values for aqua regia digestion are not available. Fe, Mg, and Mn had recoveries >60%. Similar recoveries were observed in Liaghati et al. (2003). Additional information for recovery of metals can be found in Table A.2.

A.6 Calculated natural stream water EPC_0

In nine sediments the equilibrium phosphorus concentrations were greater than the soluble reactive phosphorus concentration throughout the field season. When these cases were identified, an EPC_0 incubation was run with P spiked natural stream water. Artificial water EPC_0 and the corresponding natural water EPC_0 were fit to a type II linear regression (main text, Figure 2.5). The regression equation was used to calculate theoretical natural stream water EPC_0 values for the remaining samples (Table A.3) (McDaniel et al. 2009).

A.7 Physical sediment characterization data

Sediment data was characterized using the Laser Diffraction Technique (LA-950, Horiba Scientific) (Table A.4). Mean, median, and mode particle sizes were determined as well as the D10 and D90 values. The D10 value indicates that 10% of the sediment falls below this size while the D90 value indicates 90% of the sediment falls below the stated size. The spread is the difference between the D90 and D10 values indicating the variability of the range of particle sizes present. The % sand, % silt, and % clay fractions represent the percentage of those size

fractions present in the sediment. The % fines fraction is the % silt + % clay fraction. % fines were determined because both the silt and the clay provide important areas for P to bind (Lake and Morrison 1977).

The modified Williams (1971) method of phosphorus sequential fractionation as put forth in Ruban et al. (1999), and later modified in Ruban et al. (2001) was used to determine phosphorus bound to metals and total phosphorus. Sequential fractionation samples were run in quadruplicate at three of the sites to determine precision of the method. Results are reported in Table A.5.

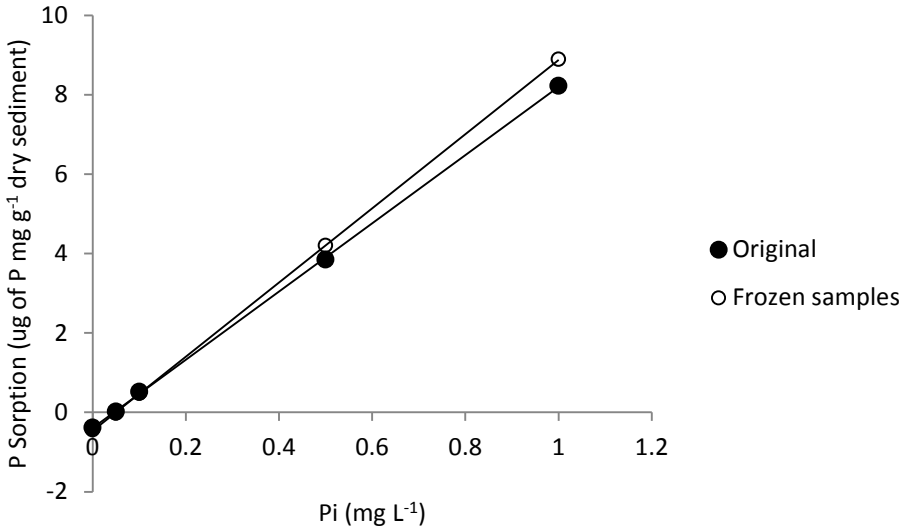

Figure A.1 Batch sorption equilibrium isotherms for site P1 run after collection and again six months later to determine differences after sediment storage using artificial water.

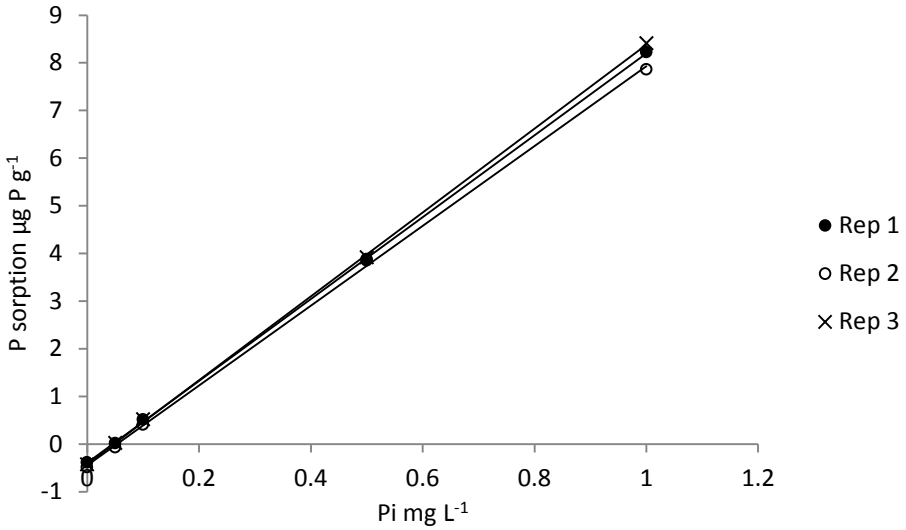

Figure A.2 Batch sorption equilibrium isotherms for three replicates of site P1 showing the reproducibility of the method using artificial water.

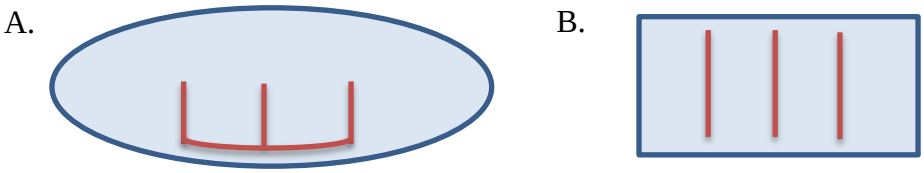

Figure A.3 Schematic of sediment sampling regime. A. Sampling regime for reservoirs. B. Sampling regime for stream pools.

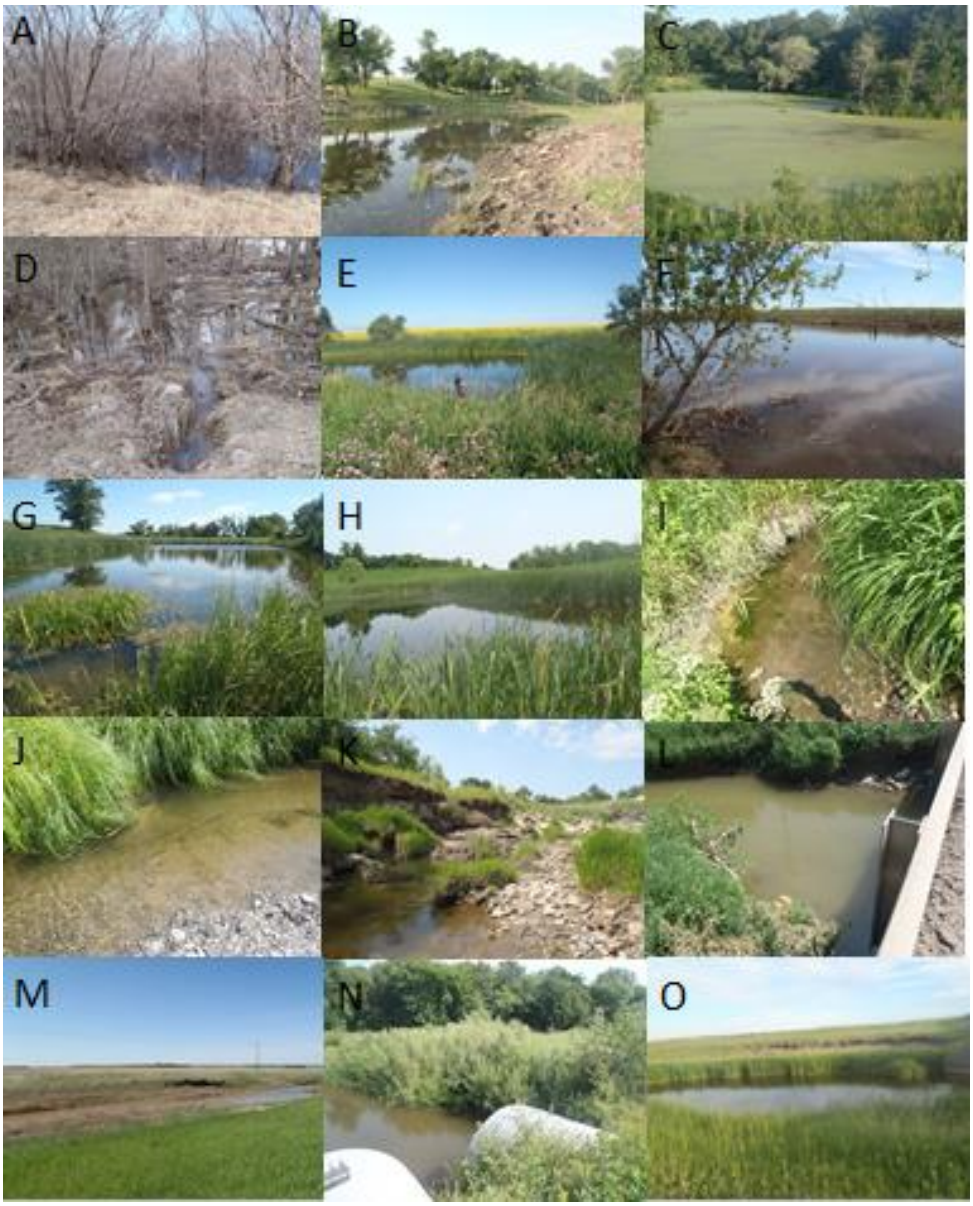

Figure A.4 Photos of study sites. A. R1 in May. B. R2 in August. C. R3 in August. D. R4 in May. E. R5 in August. F. R6 in June, G. R7 in August, H. R8 in August. I. P1 in August. J. P2 in August. K. P3 in July. L. P4 in July. M. P5 in June. N. P6 in August. O. P7 in August.

Table A.1 Measured water quality parameters Soluble Reactive Phosphorus (SRP), Total Phosphorus (TP), Alkalinity, Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) ions in collected sample, pH, dissolved oxygen (DO), % organic matter in sediment (OMS %), Dissolved Organic Carbon (DOC), Conductivity (Cond), and % fines in total sediment.

	Site	EPC_0 (mg L^{-1})	SRP (mg L^{-1})	TP (mg L^{-1})	Alkalinity (mg L^{-1})	Ca^{2+} (mg L^{-1})	Mg^{2+} (mg L^{-1})	pH	DO (mg L^{-1})	OMS %	DOC (mg L^{-1})	Cond mS m^{-1}	Fines %
May	R1	0.281	0.153	0.215	185.0	43.39	15.99	7.81	7.9	1.81	10.2	359	82.7
	R2	0.245	0.271	0.408	135.7	29.92	11.30	8.14	9.4	2.18	8.2	311	73.4
	R3	0.068	0.157	0.239	239.3	59.65	22.33	7.85	10.0	1.29	7.6	519	58.5
	R4	0.567	0.186	0.267	179.0	33.84	13.12	7.25	9.1	2.33	5.8	372	79.3
	R5	0.013	0.137	0.458	87.07	44.85	12.38	8.82	13.2	2.54	7.9	433	65.5
	R6	0.052	0.177	0.398	181.7	48.92	16.71	8.13	9.9	3.84	10.8	440	65.5
	R7	0.023	0.029	0.117	148.8	127.90	15.15	8.02	11.1	2.20	7.7	845	81.7
	R8	0.029	0.004	0.045	224.8	86.25	25.67	8.20	11.5	2.63	6.8	673	69.3
	P1	0.065	0.144	0.161	205.3	53.90	17.41	8.37	10.3	0.46	8.6	521	51.5
	P2	0.088	0.193	0.225	194.9	58.85	19.59	8.26	10.1	0.72	9.4	475	70.5
	P3	0.068	0.140	0.181	217.2	69.55	19.70	8.08	9.3	0.78	8.4	599	39.8
	P4	0.053	0.144	0.187	215.8	76.30	20.98	8.34	10.4	0.82	7.8	634	709
	P5	0.014	0.129	0.204	220.5	76.10	21.09	8.27	9.6	0.94	8.2	646	68.5
	P6	0.015	0.113	0.170	232.4	89.20	31.50	8.20	9.2	0.84	9.3	842	94.3
	P7	0.043	0.117	0.172	226.9	102.85	30.83	7.97	10.0	0.97	9.6	828	88.4
June	R1	0.177	0.288	0.335	148.2	34.90	11.03	7.35	8.5	2.35	9.7	285.5	648
	R2	0.609	0.496	0.507	113.4	33.24	8.99	6.79	9.4	3.29	13.4	272.3	63.9
	R3	0.021	0.239	0.283	224.8	60.90	20.52	6.85	14.3	1.36	8.1	388	63.4
	R4	0.383	0.169	0.175	233.7	59.26	20.37	7.73	11.2	2.57	7.2	7.21	75.5
	R5	0.016	0.356	0.467	73.27	28.03	8.06	6.71	6.8	1.86	11.8	3.48	77.9
	R6	0.027	0.319	0.457	156.1	41.21	11.34	7.16	5.8	2.13	12.6	261.1	75.2
	R7	0.007	0.166	0.272	99.9	65.28	8.26	7.04	8.7	2.14	11.9	338	77.2
	R8	0.009	0.154	0.286	132.1	60.71	9.80	7.50	9.4	2.81	10.8	280	85.7
	P1	0.067	0.208	0.239	228.6	61.74	18.43	8.08	9.2	0.41	10.2	412	41.3
	P2	0.082	0.185	0.281	196.6	52.76	14.86	7.82	9.0	0.64	9.5	372	53.9
	P3	0.065	0.169	0.240	217.4	69.93	17.34	7.68	10.4	0.59	8.7	408	43.9
	P5	0.012	0.147	0.332	208.0	81.65	19.21	7.80	9.6	0.59	8.6	487	60.2
July	R1	0.119	0.373	0.393	318.7	71.00	24.71	7.47	0.8	2.51	10.4	515	68.6
	R2	0.061	0.209	0.292	276.4	61.65	23.18	7.43	4.4	2.71	10.0	585	88.4
	R3	0.014	0.172	0.218	345.1	75.55	29.60	7.73	4.5	1.53	8.7	652	51.4
	R4	0.319	0.357	0.501	351.2	83.99	32.24	7.40	4.9	2.35	6.4	634	80.7
	R5	0.014	0.202	0.297	178.4	50.93	17.02	8.15	8.0	2.35	15.0	524	66.5

Table A.1 Measured water quality parameters. Continued.

	Site	EPC_0 (mg L^{-1})	SRP (mg L^{-1})	TP (mg L^{-1})	Alkalinity (mg L^{-1})	Ca^{2+} (mg L^{-1})	Mg^{2+} (mg L^{-1})	pH	DO (mg L^{-1})	OMS %	DOC (mg L^{-1})	Cond mS m^{-1}	Fines %
	R6	0.022	0.252	0.294	301.3	73.91	22.83	7.89	6.8	2.24	13.9	634	712
	R7	0.005	0.009		215.8	190.08	21.94	7.43	8.0	1.71	10.7	1146	80.6
	R8	0.007	0.021	0.029	286.5	107.60	29.06	7.70	6.9	3.16	10.3	814	69.9
	P1	0.044	0.098	0.120	385.6	107.99	30.59	7.93	7.6	0.43	7.9	783	48.1
	P2	0.075	0.098	0.120	281.6	74.23	20.81	7.87	9.1	0.73	6.8	598	65.0
	P3	0.046	0.094	0.389	282.3	95.31	21.78	8.16	8.9	0.57	7.0	728	29.7
	P4	0.062	0.122	0.137	302.4	110.37	26.51	8.19	7.2	0.50	6.8	0.7	30.1
	P5	0.021	0.055	0.962	294.4	112.27	29.02	8.07	7.3	0.71	8.9	920	62.7
	P6	0.014	0.010	0.661	278.2	128.23	56.96	8.33	10.1	0.81	10.1	1261	93.1
	P7	0.008	0.024	0.042	279.4	134.36	57.64	8.16	8.8	0.62	10.1	1277	93.7
August	R1	0.435	0.113	0.213	327.3	71.41	25.32	7.63	7.9	4.62	8.8	493	58.4
	R2	0.048	0.179	0.311	317.2	63.03	25.24	7.71	3.3	2.69	9.7	531	77.8
	R3	0.023	0.057	0.143	332.3	67.93	27.63	7.72	3.4	1.09	7.2	505	47.6
	R4	0.153	0.171	0.192	352.1	75.53	29.85	8.02	6.1	2.44	6.7	499	79.8
	R5	0.020	0.301	0.462	178.0	41.90	15.90	9.48	9.6	2.54	13.7	379	69.7
	R6	0.019	0.237	0.288	310.5	67.90	23.20	7.81	5.2	3.58	12.3	541	65.3
	R7	0.007	0.003	0.033	195.8	191.71	22.74	7.94	9.0	1.81	10.2	1028	82.3
	R8	0.061	0.005		239.8	72.15	35.62	8.11	8.7	2.19	9.3	624	77.7
	P1	0.046	0.060	0.086	319.8	90.79	29.18	8.37	8.9	0.64	5.5	661	36.9
	P2	0.254	0.095	0.105	305.7	72.27	23.16	8.37	10.1	0.59	6.1	569	48.2
	P3	0.047	0.086	0.100	306.0	91.06	23.04	8.36	9.8	0.77	5.9	646	54.6
	P4	0.236	0.097	0.139	297.8	101.82	24.14	8.26	9.0	0.42	5.9	686	38.4
	P5	0.023	0.038	0.099	291.7	114.76	28.29	8.14	9.3	0.72	5.1	822	78.8
	P6	0.013	0.039	0.096	262.0	120.08	67.33	8.11	8.1	0.69	10.4	1200	90.9
	P7	0.028	0.017	0.040	256.0	134.47	83.53	7.94	8.6	0.93	11.6	1425	88.7

Table A.2 PACS-2 certified reference amounts (g kg^{-1}) ± Standard Deviation, recovery in the present study, % Recovery and % Precision of the aqua regia digestion.

Element	Certified (PACS-2)	Recovered (g kg^{-1})	Recovery (%)	Precision (%CV)
Fe	40.9 ± 0.6	29.9 ± 1.7	73.1	3.1
Mg	14.7 ± 1.3	8.9 ± 0.5	60.5	0.43
Mn	0.44 ± 0.7	0.52 ± 0.05	118	2.25

Table A.3 Results of artificial water EPC_0 compared to calculated natural stream water EPC_0 (using type II regression analysis, see Figure 2.5, main text).

Month	subject	Aw ($mg\ L^{-1}$)	Sw ($mg\ L^{-1}$)
May	R1	0.281	0.212
	R2	0.245	0.183
	R3	0.068	0.042
	R4	0.567	0.441
	R5	0.013	-0.002
	R6	0.052	0.029
	R7	0.023	0.006
	R8	0.029	0.010
	P1	0.065	0.040
	P2	0.088	0.057
	P3	0.068	0.042
	P4	0.053	0.030
	P5	0.014	-0.001
	P6	0.015	-0.001
	P7	0.043	0.021
June	R1	0.177	0.129
	R3	0.021	0.004
	R5	0.016	0.000
	R6	0.027	0.009
	R7	0.007	-0.007
	R8	0.009	-0.006
	P1	0.067	0.041
	P2	0.082	0.053
	P3	0.065	0.040
	P5	0.012	-0.003
July	R1	0.119	0.083
	R2	0.061	0.036
	R3	0.014	-0.001
	R4	0.319	0.242
	R5	0.014	-0.001
	R6	0.022	0.005
	R7	0.005	-0.009
	R8	0.007	-0.007
	P1	0.044	0.023
	P2	0.075	0.048
	P3	0.046	0.024
	P4	0.062	0.037
	P5	0.021	0.004
	P6	0.014	-0.001
	P7	0.008	-0.006
August	R2	0.048	0.025
	R3	0.023	0.006
	R4	0.153	0.110
	R5	0.020	0.004
	R6	0.019	0.003
	P3	0.047	0.025
	P6	0.013	-0.002

Table A.4 Physical sediment characterization data. Median particle size 10% of sediment lies below the D10 value, 90% of sediment lies below the D90 value, % of sediment as fines (%silt+%clay) and mode sediment size.

Site	Date	Median	Mean	Mode	D10	D90	Spread	%sand	%fines	%silt	%clay
R1	May	29.671	40.660	54.874	4.087	87.179	83.092	17.344	82.657	79.277	3.380
R2	May	30.382	48.845	55.084	3.733	116.216	112.483	26.564	73.439	69.432	4.007
R3	May	46.902	77.414	63.084	5.360	206.275	200.915	41.541	58.461	55.792	2.669
R4	May	23.561	41.293	54.978	3.395	99.898	96.503	20.710	79.289	74.861	4.428
R5	May	33.000	55.936	72.370	3.471	144.030	140.559	34.529	65.471	61.564	3.907
R6	May	37.225	51.975	63.190	3.993	117.628	113.635	34.495	65.504	61.471	4.033
R7	May	24.009	37.811	55.054	2.553	89.602	87.049	18.298	81.702	73.962	7.740
R8	May	27.050	102.881	54.984	2.933	376.902	373.969	30.730	69.270	62.717	6.553
P1	May	60.895	167.117	423.620	4.440	497.404	492.964	48.526	51.470	47.986	3.484
P2	May	45.508	313.470	951.011	3.381	1064.609	1061.228	29.524	70.474	64.519	5.955
P3	May	108.087	323.017	1078.077	4.825	1022.307	1017.482	60.251	39.752	35.564	4.188
P4	May	30.100	51.184	55.107	3.226	132.829	129.603	29.114	70.886	64.944	5.942
P5	May	33.549	119.763	48.119	3.545	361.335	357.790	31.493	68.509	63.755	4.754
P6	May	5.138	16.066	4.178	0.404	47.753	47.349	5.732	94.266	61.748	32.518
P7	May	7.596	22.731	3.192	1.454	66.749	65.295	11.631	88.374	69.612	18.762
R1	June	39.117	165.020	48.173	5.212	724.922	719.710	35.202	64.796	62.240	2.556
R2	June	41.288	115.865	55.152	5.820	304.292	298.472	36.069	63.930	61.778	2.152
R3	June	44.138	75.894	63.166	4.881	202.993	198.112	36.629	63.370	60.479	2.891
R4	June	25.922	43.962	55.095	3.844	105.873	102.029	24.487	75.513	71.849	3.664
R5	June	22.360	42.903	62.996	2.828	109.343	106.515	22.114	77.886	70.575	7.311
R6	June	30.922	40.203	55.135	3.623	88.321	84.698	24.803	75.199	70.587	4.612
R7	June	27.875	39.422	62.962	2.970	91.544	88.574	22.754	77.247	71.486	5.761
R8	June	18.845	31.684	55.117	2.687	78.233	75.546	14.307	85.696	78.182	7.514
P1	June	110.477	256.859	484.241	4.818	694.905	690.087	58.709	41.296	36.900	4.396
P2	June	195.978	594.347	1413.024	4.435	1597.555	1593.120	46.138	53.867	49.713	4.154
P3	June	102.438	168.549	281.038	4.944	430.610	425.666	56.111	43.889	39.742	4.147
P5	June	42.938	141.699	55.137	3.918	468.511	464.593	39.766	60.237	56.341	3.896
R1	July	34.945	56.845	55.159	4.126	145.305	141.179	31.414	68.586	64.645	3.941
R2	July	23.156	32.889	48.253	3.769	74.793	71.024	11.611	88.388	84.683	3.705
R3	July	62.800	183.717	63.121	6.783	589.966	583.183	48.631	51.373	49.092	2.281
R4	July	22.559	39.274	48.107	3.489	93.646	90.157	19.335	80.668	75.992	4.676
R5	July	29.280	52.799	72.339	3.196	137.581	134.385	33.471	66.526	62.280	4.246
R6	July	35.567	47.081	63.091	3.473	104.443	100.970	28.829	71.168	66.410	4.758
R7	July	25.354	36.094	55.226	2.811	84.256	81.445	19.434	80.566	73.359	7.207
R8	July	29.185	64.051	55.175	3.208	109.574	106.366	30.061	69.940	64.187	5.753
P1	July	90.948	246.603	550.473	4.580	654.362	649.782	51.929	48.069	44.515	3.554
P2	July	25.943	143.924	62.934	2.986	571.788	568.802	34.964	65.039	60.183	4.856
P3	July	266.034	327.758	557.793	5.963	747.543	741.580	70.328	29.672	27.351	2.321
P4	July	269.625	304.656	550.739	7.150	676.472	669.322	69.914	30.087	28.073	2.014
P5	July	43.620	114.854	55.148	3.753	368.046	364.293	37.291	62.709	58.217	4.492
P6	July	5.629	19.913	4.182	0.461	49.428	48.967	6.882	93.119	69.183	23.936
P7	July	7.863	20.113	3.644	1.553	56.126	54.573	6.288	93.711	80.036	13.675
R1	August	44.594	124.507	55.063	4.865	424.946	420.081	41.621	58.379	55.752	2.627
R2	August	26.786	40.434	55.092	3.659	93.907	90.248	22.200	77.797	74.081	3.716
R3	August	61.343	141.451	63.054	5.597	413.607	408.010	52.436	47.563	44.912	2.651
R4	August	21.748	37.142	48.076	3.274	89.189	85.915	20.154	79.846	74.416	5.430
R5	August	30.899	49.685	72.105	3.641	121.922	118.281	30.333	69.665	65.625	4.040
R6	August	40.681	59.061	72.111	3.213	143.200	139.987	34.701	65.301	60.556	4.745
R7	August	21.055	32.090	55.083	2.435	78.205	75.770	17.685	82.315	73.532	8.783
R8	August	20.134	106.569	54.880	2.370	174.457	172.087	22.291	77.710	67.942	9.768
P1	August	389.968	522.209	1080.818	5.508	1281.148	1275.640	63.071	36.932	33.025	3.907
P2	August	78.432	323.411	723.475	3.305	910.504	907.199	51.805	48.193	42.315	5.878

Table A.4 Physical sediment characterization data continued.

Site	Date	Median	Mean	Mode	D10	D90	Spread	%sand	%fines	%silt	%clay
P3	August	54.412	112.481	244.736	3.933	319.602	315.669	45.358	54.643	50.915	3.728
P4	August	173.986	233.709	322.593	7.757	559.021	551.264	61.650	38.352	35.168	3.184
P5	August	23.477	41.546	48.115	2.992	105.373	102.381	21.178	78.823	72.355	6.468
P6	August	5.526	18.384	3.653	0.422	55.729	55.307	9.102	90.897	65.284	25.613
P7	August	8.894	23.667	3.185	1.517	66.501	64.984	11.328	88.670	70.185	18.485

Table A.5 Phosphorus fractions (mg P g^{-1} dry sediment) of three sites run in quadruplicate.

	Metal Oxide-P	Calcium-P	Total Phosphorus
	mg P g^{-1} dry sediment		
R3	0.096	0.033	0.249
	0.106	0.039	0.255
	0.092	0.032	0.300
	0.089	0.037	0.260
R1	0.107	0.031	0.823
	0.089	0.032	0.865
	0.086	0.026	0.863
	0.091	0.027	0.749
R2	0.080	0.104	0.577
	0.081	0.106	0.529
	0.086	0.107	0.501
	0.088	0.099	0.485

A.8 Literature Cited

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APPENDIX B

B.1 Sediment Fractionation

The modified Williams (1971) method as put forth in Ruban et al. (1999), and later modified in Ruban et al. (2001) was used to determine both HCl extractable P, commonly referred to as Calcium bound P (Calcium-P) and metal oxide bound P, P bound to Fe. Averages and standard deviations of each P fraction for all four reservoirs are found in Table B.1.

B.2 Supporting data for short term deployments

Summary data for short term deployments are presented in the main text; however, comprehensive point data for dissolved oxygen (DO), pH, and hand measured SRP and TP as well as high frequency Cycle-P data gathered from June, July, and August deployments are reported here (Figures B.2-5 and Tables B.2-9).

B.3 Linearly interpolated data for wavelet analysis

Temperature and Cycle-P data were gathered at different sampling frequencies. In order to complete wavelet analysis, both sets of data needed to linearly interpolated to the same frequency. To illustrate the accurate fit of the interpolated data, sampled data has been graphed with the interpolated data overlaid for R2 (Figure B.6), R3-1 (Figure B.7), and R3-2 (Figure B.8).

B.4 Total phosphorus (TP) methods

Unfiltered water samples (35mL) were collected in 50 mL glass vials, kept on ice, and analyzed within 30 days for TP analysis, via the molybdate blue method (Murphy and Riley 1962) using a UV-1601PC UV-Visible spectrophotometer (Shimadzu, Laval, QC). TP samples were digested with a 3% potassium persulfate solution in an autoclave for 45 minutes at 121 °C before analysis (Manzel and Corwin 1965, Wetzel and Likens 1991).

B.5 Additional photos

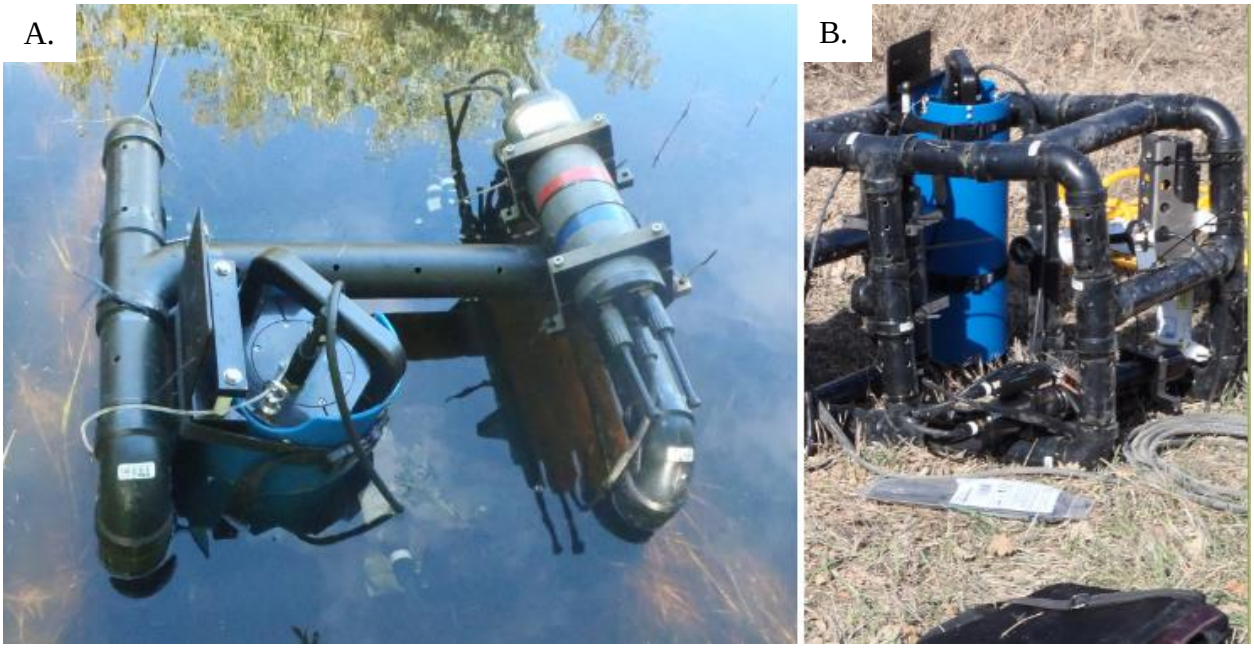


Figure B.1 Sensor deployment structure. A. Structure in the water showing 75% submersion of Cycle-P (blue instrument). B. Structure outside of the water showing vertical orientation of the blue Cycle-P.

Table B.1 Average values ± one standard deviation of Calcium bound P and metal oxide bound P in reservoirs R1, R2, R3, R8. Extractions were completed by the Modified Williams Method as described in section 2.2.4.2.

	Calcium-P	Metal Oxide-P
	(mg P g^{-1})	
R1	0.030 ± 0.005	0.094 ± 0.011
R2	0.104 ± 0.003	0.085 ± 0.004
R3	0.034 ± 0.002	0.092 ± 0.011
R8	0.061 ± 0.009	0.012 ± 0.002

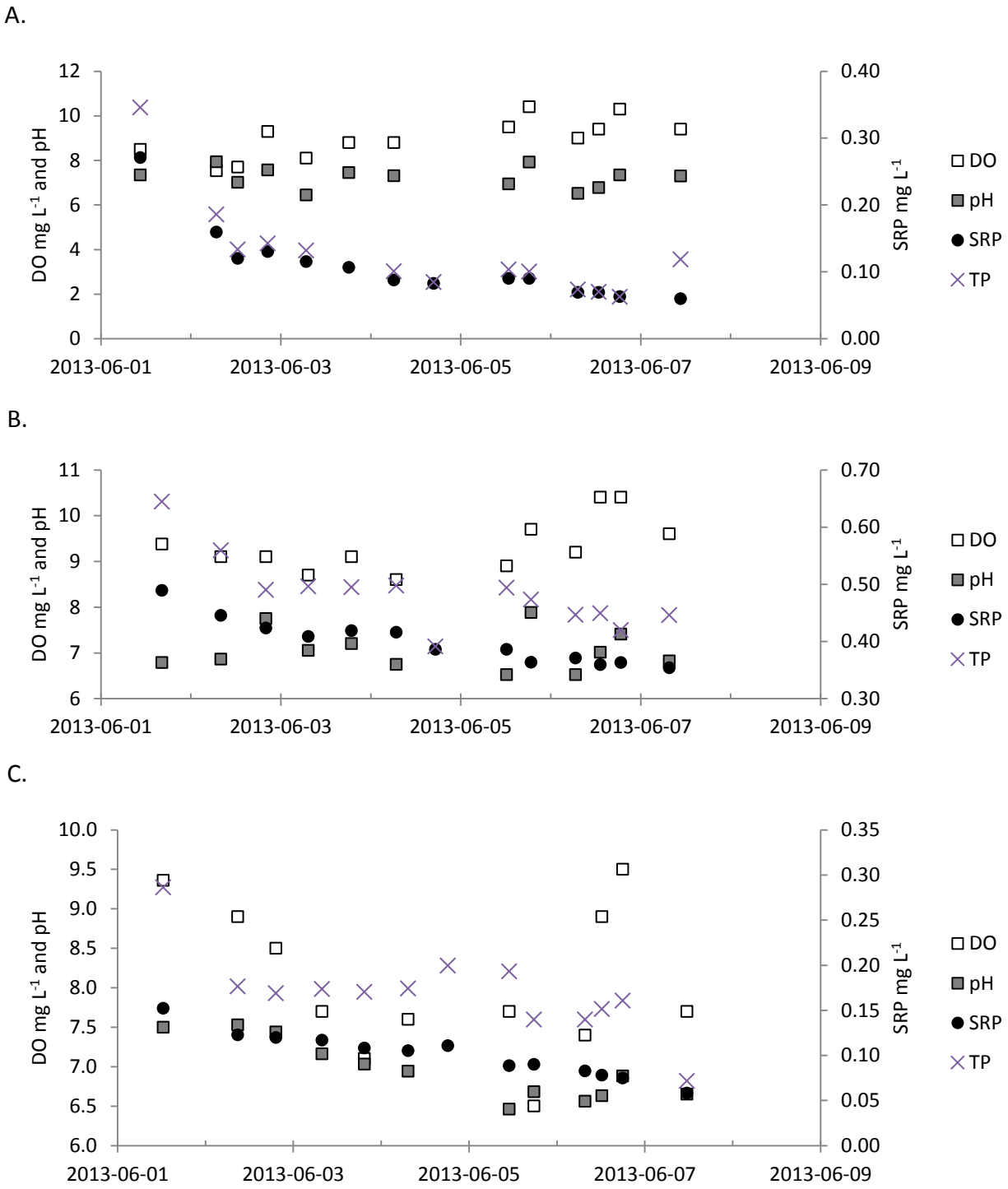


Figure B.2 Scatter plots of hand sampled dissolved oxygen (DO), pH, total phosphorus (TP) and, soluble reactive phosphorus (SRP) data for short term deployments in June. A. Reservoir 1. B. Reservoir 2. C. Reservoir 8. Tick marks indicate midnight for each day of deployment.

Table B.2 Hand sampled soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved oxygen (DO), and pH data from R1 June short-term deployment.

Date	Time	SRP mg L^{-1}	TP mg L^{-1}	DO mg L^{-1}	pH
2013-06-01	1030	0.271	0.346	8.5	7.35
2013-06-02	650	0.159	0.186	7.5	7.91
2013-06-02	1230	0.120	0.133	7.7	7.01
2013-06-02	2030	0.130	0.143	9.3	7.57
2013-06-03	645	0.115	0.132	8.1	6.45
2013-06-03	1810	0.107		8.8	7.45
2013-06-04	610	0.088	0.101	8.8	7.31
2013-06-04	1645	0.083	0.084		
2013-06-05	1250	0.090	0.103	9.5	6.94
2013-06-05	1815	0.090	0.100	10.4	7.92
2013-06-06	715	0.069	0.073	9	6.52
2013-06-06	1250	0.069	0.070	9.4	6.78
2013-06-06	1825	0.063	0.062	10.3	7.35
2013-06-07	1040	0.060	0.118	9.4	7.3

Table B.3 R2 hand sampled soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved oxygen (DO), and pH data from June short-term deployment.

Date	Time	SRP mg L^{-1}	TP mg L^{-1}	DO mg L^{-1}	pH
2013-06-01	1615	0.489	0.644	9.4	6.79
2013-06-02	800	0.445	0.559	9.1	6.86
2013-06-02	2000	0.423	0.490	9.1	7.75
2013-06-03	720	0.409	0.496	8.7	7.05
2013-06-03	1850	0.419	0.495	9.1	7.2
2013-06-04	650	0.416	0.498	8.6	6.75
2013-06-04	1715	0.386	0.391		
2013-06-05	1215	0.386	0.494	8.9	6.52
2013-06-05	1845	0.364	0.473	9.7	7.88
2013-06-06	640	0.371	0.446	9.2	6.52
2013-06-06	1315	0.359	0.449	10.4	7.01
2013-06-06	1845	0.363	0.420	10.4	7.41
2013-06-07	740	0.354	0.446	9.6	6.82

Table B.4 R8 hand sampled soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved oxygen (DO), and pH data from June short-term deployment.

Date	Time	SRP	TP	DO	pH
		mg L^{-1}	mg L^{-1}	mg L^{-1}	
2013-06-01	1230	0.152	0.286	9.4	7.50
2013-06-02	850	0.123	0.176	8.9	7.53
2013-06-02	1915	0.120	0.169	8.5	7.44
2013-06-03	750	0.117	0.173	7.7	7.16
2013-06-03	1925	0.108	0.170	7.1	7.03
2013-06-04	720	0.105	0.174	7.6	6.94
2013-06-04	1815	0.111	0.199		
2013-06-05	1100	0.088	0.193	7.7	6.46
2013-06-05	1745	0.090	0.139	6.5	6.68
2013-06-06	740	0.083	0.139	7.4	6.56
2013-06-06	1215	0.078	0.151	8.9	6.63
2013-06-06	1800	0.075	0.161	9.5	6.88
2013-06-07	1130	0.058	0.072	7.7	6.65

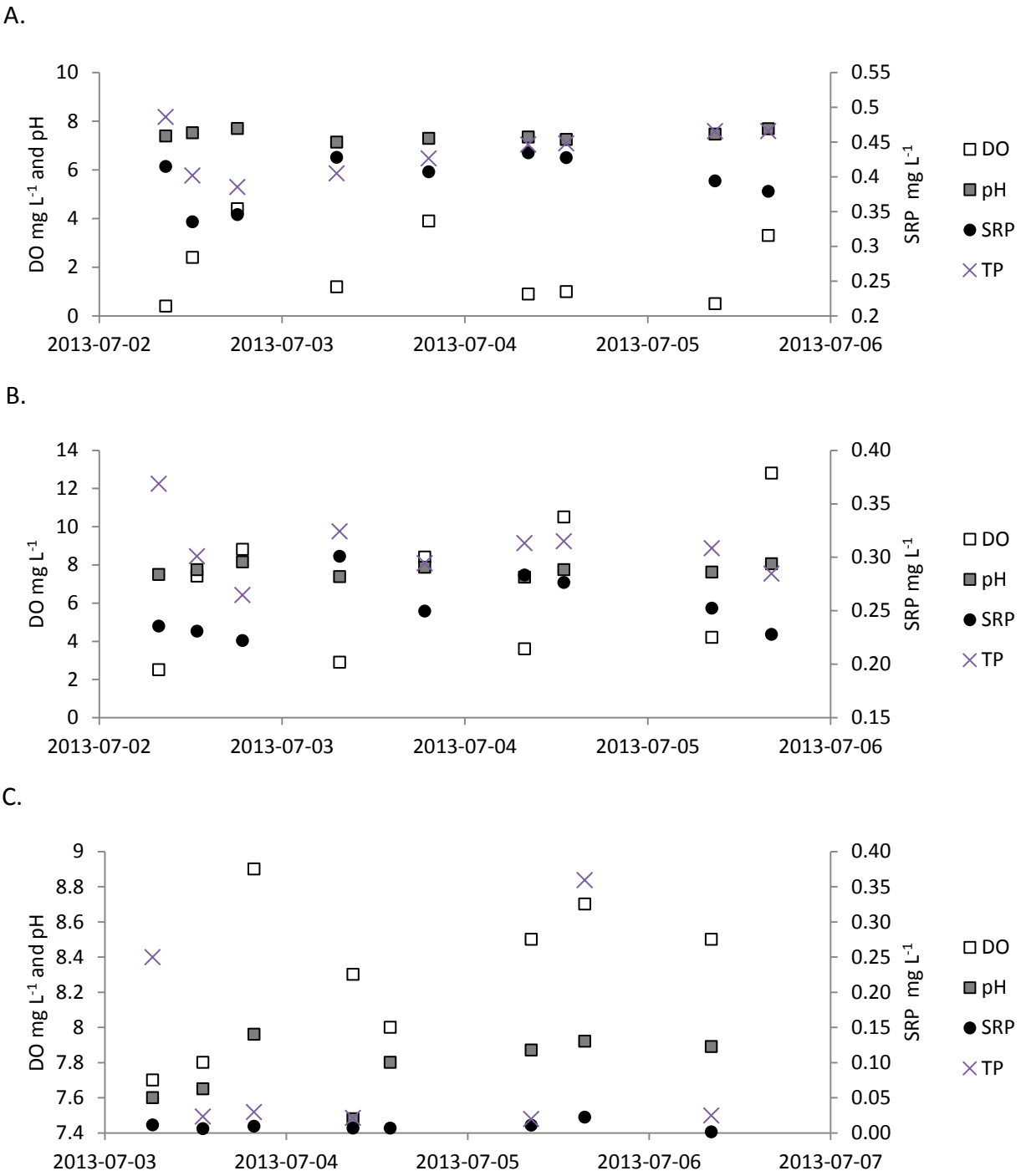


Figure B.3 Scatter plots of hand sampled dissolved oxygen (DO), pH, total phosphorus (TP) and, soluble reactive phosphorus (SRP) data for short term deployments in July. A. Reservoir 1. B. Reservoir 2. C. Reservoir 8. Tick marks indicate midnight for each day of deployment.

Table B.5 R1 hand sampled soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved oxygen (DO), and pH data from July short-term deployment.

Date	Time	SRP	TP	DO	pH
		mg L^{-1}	mg L^{-1}	mg L^{-1}	
2013-07-02	845	0.486	0.486	0.4	7.39
2013-07-02	1215	0.335	0.402	2.4	7.52
2013-07-02	1810	0.345	0.385	4.4	7.69
2013-07-03	710	0.428	0.405	1.2	7.14
2013-07-03	1915	0.407	0.426	3.9	7.29
2013-07-04	820	0.434	0.446	0.9	7.34
2013-07-04	1320	0.428	0.448	1	7.24
2013-07-05	850	0.394	0.465	0.5	7.47
2013-07-05	1550	0.379	0.465	3.3	7.68

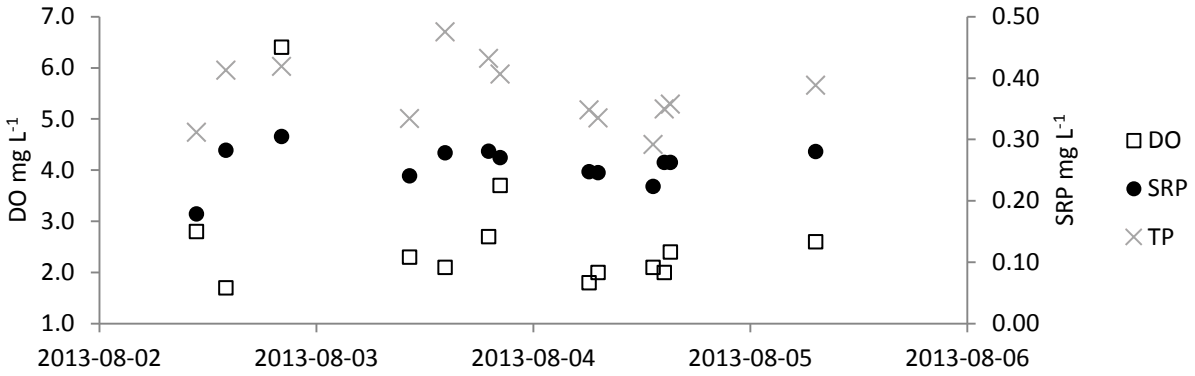
Table B.6 R2 hand sampled soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved oxygen (DO), and pH data from July short-term deployment.

Date	Time	SRP	TP	DO	pH
		mg L^{-1}	mg L^{-1}	mg L^{-1}	
2013-07-02	7:50	0.235	0.369	2.5	7.49
2013-07-02	12:50	0.231	0.301	7.4	7.74
2013-07-02	18:50	0.222	0.264	8.8	8.15
2013-07-03	7:35	0.301	0.324	2.9	7.37
2013-07-03	18:45	0.249	0.294	8.4	7.87
2013-07-04	7:50	0.283	0.313	3.6	7.35
2013-07-04	13:00	0.276	0.315	10.5	7.74
2013-07-05	8:25	0.252	0.308	4.2	7.62
2013-07-05	16:15	0.228	0.285	12.8	8.05

Table B.7 R8 hand sampled soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved oxygen (DO), and pH data from July short-term deployment.

Date	Time	SRP	TP	DO	pH
		mg L^{-1}	mg L^{-1}	mg L^{-1}	
2013-07-03	620	0.011	0.249	7.7	7.6
2013-07-03	1300	0.006	0.023	7.8	7.65
2013-07-03	1945	0.009	0.029	8.9	7.96
2013-07-04	850	0.007	0.021	8.3	7.48
2013-07-04	1345	0.007		8	7.8
2013-07-05	930	0.011	0.020	8.5	7.87
2013-07-05	1530	0.022	0.359	8.7	7.92
2013-07-06	815	0.001	0.024	8.5	7.89

A.



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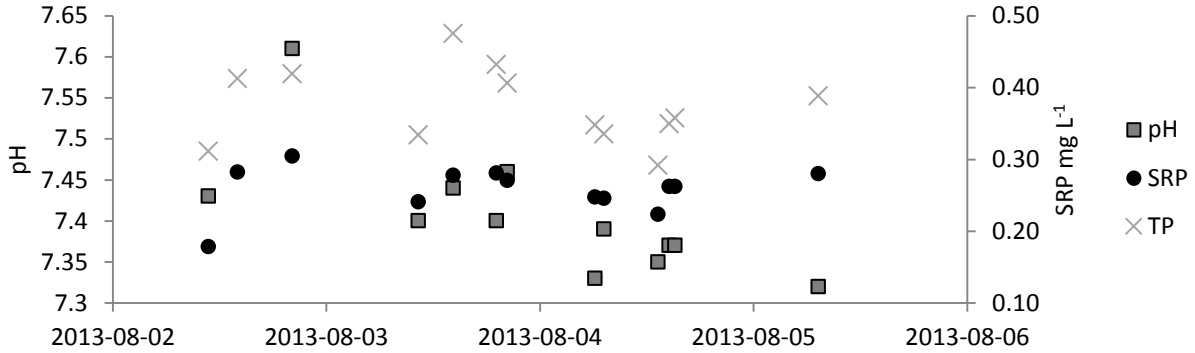
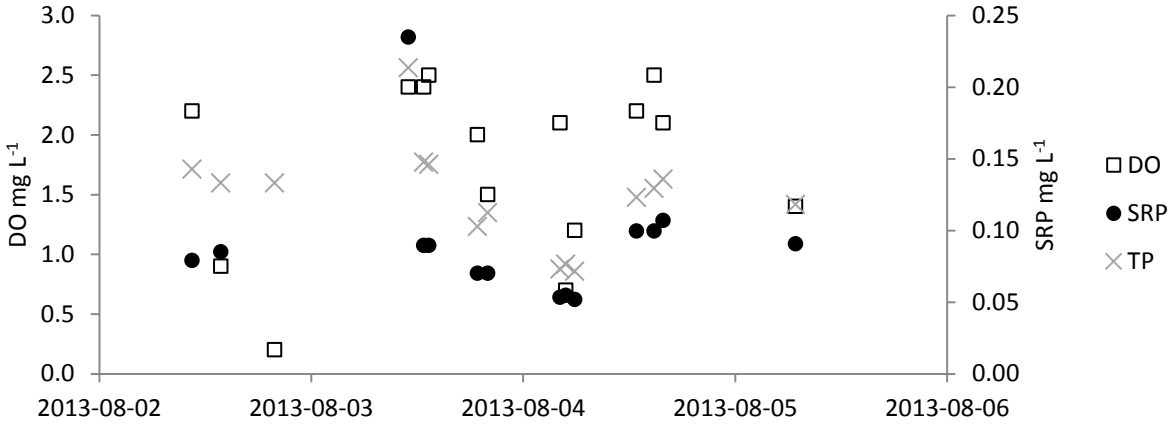


Figure B.4 Scatter plots of hand sampled dissolved oxygen (DO), pH, total phosphorus (TP) and, soluble reactive phosphorus (SRP) data for short term deployments for Reservoir 2 in August. A. DO, TP, and SRP in Reservoir 2. B. pH, TP, and SRP in Reservoir 2. Tick marks indicate midnight for each day of deployment.

A.



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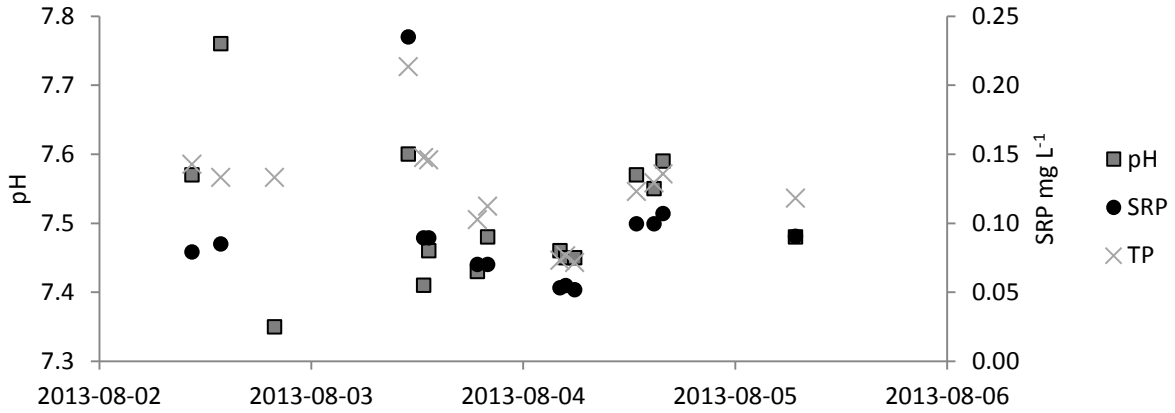


Figure B.5 Scatter plots of hand sampled dissolved oxygen (DO), pH, total phosphorus (TP), and soluble reactive phosphorus (SRP) data for short term deployments for Reservoir 3 in August. A. DO, TP, and SRP in Reservoir 3. B. pH, TP, and SRP in Reservoir 3. Tick marks indicate midnight for each day of deployment.

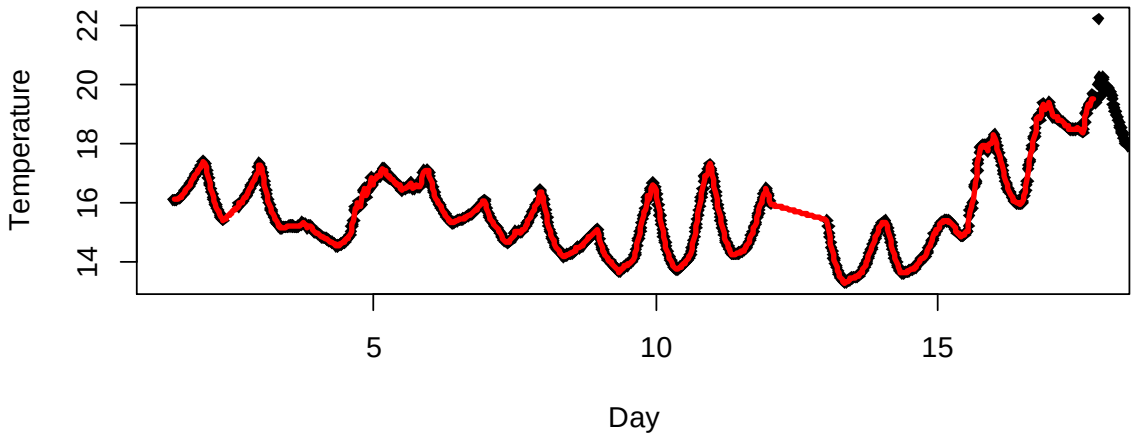
Table B.8 R2 hand sampled soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved oxygen (DO), and pH data from August short-term deployment.

Date	Time	SRP	TP	DO	pH
		mg L^{-1}	mg L^{-1}	mg L^{-1}	
2013-08-02	1045	0.178	0.311	2.8	7.43
2013-08-02	1400	0.282	0.412	1.7	7.77
2013-08-02	2010	0.305	0.419	6.4	7.61
2013-08-03	1020	0.241	0.334	2.3	7.40
2013-08-03	1415	0.278	0.475	2.1	7.44
2013-08-03	1905	0.281	0.432	2.7	7.40
2013-08-03	2020	0.270	0.406	3.7	7.46
2013-08-04	610	0.247	0.348	1.8	7.33
2013-08-04	710	0.246	0.335	2	7.39
2013-08-04	1315	0.223	0.292	2.1	7.35
2013-08-04	1430	0.262	0.349	2	7.37
2013-08-04	1510	0.262	0.357	2.4	7.37
2013-08-05	715	0.280	0.388	2.6	7.32
2013-08-06	1000	0.213	0.256	0.5	7.28
2013-08-07	945	0.188		4.5	7.46
2013-08-08	900	0.118		3.3	7.41
2013-08-09	845	0.234		2.8	7.31
2013-08-10	1000	0.281		2.6	7.41

Table B.9 R3 hand sampled soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved oxygen (DO), and pH data from August short-term deployment.

Date	Time	SRP	TP	DO	pH
		mg L^{-1}	mg L^{-1}	mg L^{-1}	
2013-08-02	1030	0.079	0.143	2.2	7.57
2013-08-02	1345	0.085	0.133	0.9	
2013-08-02	1950		0.133	0.2	7.35
2013-08-03	1100	0.235	0.213	2.4	7.60
2013-08-03	1245	0.089	0.148	2.4	7.41
2013-08-03	1320	0.089	0.146	2.5	7.46
2013-08-03	1850	0.070	0.103	2.0	7.47
2013-08-03	2000	0.070	0.112	1.5	7.48
2013-08-04	410	0.053	0.073	0.9	7.46
2013-08-04	450	0.055	0.076	1.0	7.45
2013-08-04	550	0.052	0.071	1.2	7.45
2013-08-04	1250	0.010	0.123	2.2	7.57
2013-08-04	1450	0.010	0.129	2.5	7.55
2013-08-04	1550	0.107	0.136	2.1	7.59
2013-08-05	650	0.091	0.118	1.4	7.48
2013-08-06	930	0.120	0.158		7.36
2013-08-07	900	0.056		2	7.51
2013-08-08	930	0.050		1.9	7.58
2013-08-09	800	0.041		1.1	7.47
2013-08-10	930	0.113		0.9	7.53

A.



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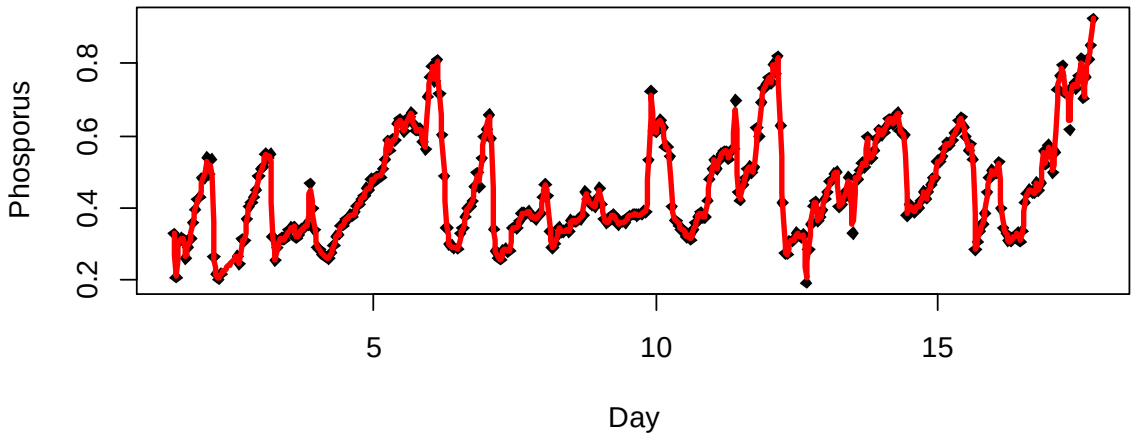
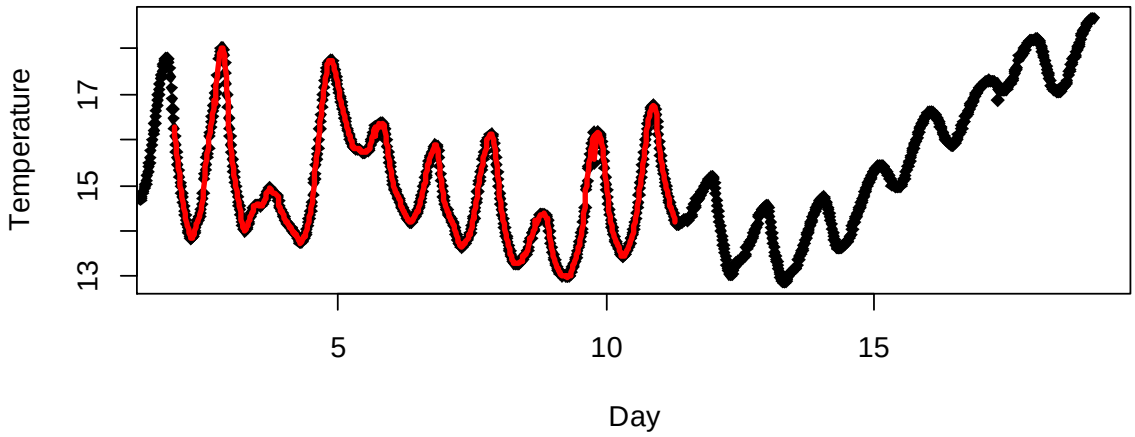


Figure B.6 Collected data (black) and linearly interpolated data (red) for Reservoir 2 (R2). A. Original temperature (ºC) data (black) for Reservoir 2(R2) overlaid with linearly interpolated temperature data (red) for the month of August. B. Original soluble reactive phosphorus mg L^{-1} (SRP) for Reservoir 2 (R2) data overlaid with linearly interpolated SRP data.

A.



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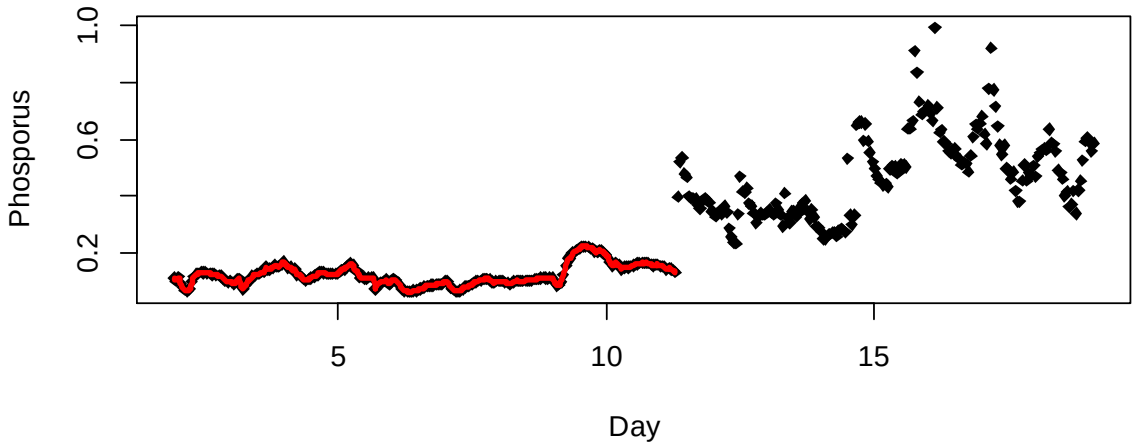

Figure B.7 Collected data (black) for entirety of R3 deployment and linearly interpolated data (red) for R3-1 (August 3-12). A. Original temperature (ºC) data for Reservoir 3 deployment 1 (R3-1) (black) overlaid with linearly interpolated temperature data (red) for the month of August. B. Original soluble reactive phosphorus mg L^{-1} (SRP) for Reservoir 3 deployment 1 (R3-1) data overlaid with linearly interpolated SRP data.

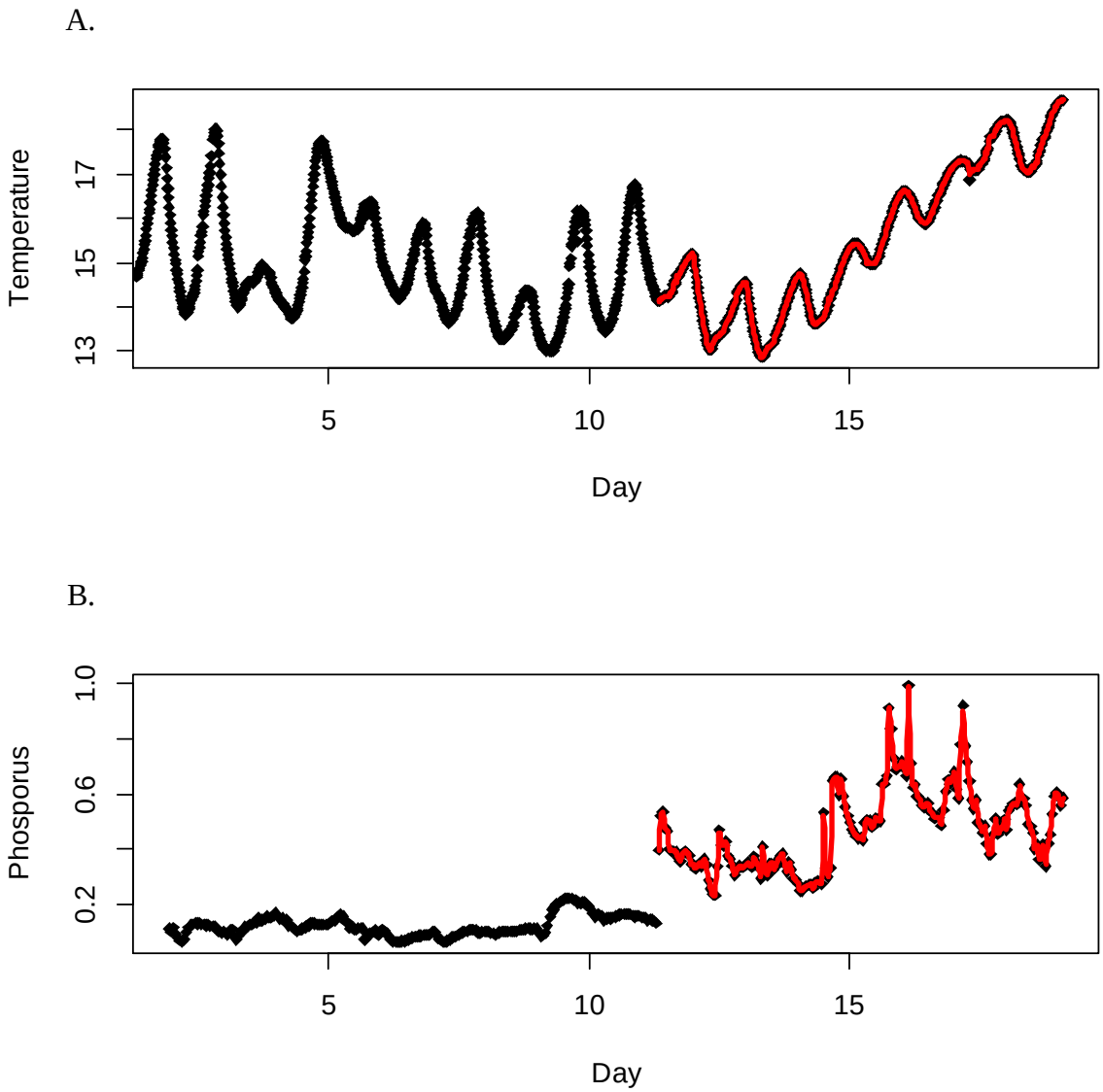

Figure B.8 Collected data (black) for entirety of deployment and linearly interpolated data (red) for R3-2 (August 12-20). A. Original temperature (ºC) data for Reservoir 3 deployment 2 (R3-2) (black) overlaid with linearly interpolated temperature data (red) for the month of August. B. Original soluble reactive phosphorus mg L^{-1} (SRP) for Reservoir 3 deployment 2 (R3-2) data overlaid with linearly interpolated SRP data.

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